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# The Role of Particulate Matter in the Fate of Contaminants in Aquatic Ecosystems

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**R.J. Allan**

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Cover photograph—

The Niagara River entering Lake Ontario at Niagara-on-the-Lake. *(Courtesy of W.G. Booth, Aquatic Ecology Division, National Water Research Institute)*

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# The Role of Particulate Matter in the Fate of Contaminants in Aquatic Ecosystems*

**R.J. Allan**

*Invited Keynote presentations by Dr. R.J. Allan at the Second Water Management Symposium held at the Chisholm Institute of Technology, Melbourne, Australia, in November 1983. Dr. Allan is the Chief of the Environmental Contaminants Division, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada L7R 4A6.

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# Foreword

These two companion papers are not meant to be exhaustive reviews of all the published literature that may have direct or indirect bearing on the role of particulates in the fate of contaminants. The intention here is to illustrate the overall state of the art, the factors and processes involved in the role of particulates in the fate of contaminants in aquatic ecosystems, and to highlight points of contention or hypotheses for testing. The vast subject area involved restricts individual researchers, or even global networks of experts, to manageable units of investigation. There are still major gaps in knowledge, especially at the interfaces between various research disciplines.

These two papers were invited Keynote presentations at a conference entitled "The Role of Particulate Matter in the Fate of Pollutants," held at the Chisholm Institute of Technology in Melbourne, Australia, November 21 and 22, 1983. This report (NWRI Contribution 84-16) contains all the figures and tables presented as slides at the conference. By necessity, shorter papers, in which only a few figures and tables can be included, will appear in the Proceedings of the Conference, edited by Dr. B.T. Hart, Executive Director, Water Studies Centre, Chisholm Institute of Technology, Melbourne, Australia.

# Avant-propos

Ces deux études complémentaires ne sont pas destinées à être un examen exhaustif de toutes les publications qui peuvent porter directement ou non sur le rôle des particules dans le devenir des contaminants, mais plutôt à montrer l'état actuel des techniques, les facteurs et les processus qui participent à ce rôle dans les écosystèmes aquatiques et à proposer à la vérification les points controversés ou les hypothèses. La grandeur du domaine fait que les chercheurs et même les réseaux de spécialistes à l'échelle du globe doivent se contenter de prospecter les domaines qu'ils peuvent. Il subsiste des lacunes importantes dans les connaissances, notamment au point de contact des diverses disciplines de la recherche.

Les deux études ont été sollicitées pour donner le ton à une conférence sur le rôle des particules dans le devenir des polluants, tenue à l'Institut de technologie Chisholm, à Melbourne, en Australie, les 21 et 22 novembre 1983. Le présent rapport (contribution 84-16 de l'INRE) comprend toutes les figures et tous les tableaux présentés en diaporama à la conférence. À cause de contraintes inévitables, les communications plus courtes, qui ne peuvent comprendre que quelques figures et tableaux, paraîtront dans les comptes rendus de la conférence, préparés par B.T. Hart, Directeur administratif du centre des études de l'eau, Institut de technologie Chisholm.

# Acknowledgments

Dr. B.G. Oliver, National Water Research Institute (NWRI) and Messrs. D. Warry, K. Kuntz and R. McCrea of the Inland Waters Directorate, Ontario Region (IWD-OR), generously provided me with reports from which I could extract information to demonstrate some of the concepts and hypotheses discussed. I am also grateful to Dr. Oliver for access to his reprint collection. Dr. J.H. Carey (NWRI) and Mr. R. McCrea (IWD-OR) discussed key points and issues with me. Another generous source of help in the form of reprints and preprints was Prof. Dr. U. Förstner of Hamburg/Harburg Technical University, Hamburg, West Germany.

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# Abstract

A review in 1978 revealed that much of the information on suspended particulate chemistry was limited to phosphorus and its forms. For bottom sediments, in addition to phosphorus data, there was much information on toxic metals but scant information on toxic organics. In the last five years, major steps have been taken in understanding speciation of metals in aquatic ecosystems, especially by application of selective extraction procedures to bottom sediments. In Canada, study of the fate of toxic organometallics and organics in polluted rivers and lakes has involved detailed investigations of transport and burial processes. In this review, two Canadian sites were selected for demonstration purposes: (1) the Niagara River-Lake Ontario system for toxic metals and organics, especially the latter, and (2) the English-Wabigoon River system for mercury and methylmercury. As a preliminary to the examination of transport and burial of contaminants in these systems, the state of the art in (1) toxic metal speciation in aquatic ecosystems and (2) sorption of toxic organic chemicals by particulate matter is reviewed. The data presented on particulate and aqueous phase chemistry rely partly on the development and recent field use of high-speed centrifuges and large-volume aqueous liquid/liquid extractors. The latter have enabled better estimates of the importance of the aqueous phase in the transport of toxic organic chemicals. Burial of toxic metals and organics is discussed with emphasis on (1) bottom sediment toxic metal speciation and (2) the use of age-dated sediment cores to reflect historical changes in organic contaminant loadings.

# Résumé

Une étude réalisée en 1978 avait montré qu'une grande partie des renseignements sur la chimie des particules en suspension se limitait au phosphore et à ses composés. Pour les sédiments de fond, en plus des données sur le phosphore, on disposait de nombreuses données sur les métaux toxiques mais de très peu d'informations sur les substances organiques toxiques. Au cours des cinq dernières années, des progrès importants ont été réalisés dans l'étude de la spéciation des métaux dans les écosystèmes aquatiques, grâce en particulier à l'application aux sédiments de fond des méthodes d'extraction sélective. Au Canada, des recherches détaillées ont été faites sur le transport et l'enfouissement afin d'étudier le sort des substances organiques et organométalliques toxiques dans les rivières et les lacs pollués. Deux sites canadiens ont été essentiellement utilisés pour les démonstrations de la présente étude, ce sont : 1) le réseau constitué par la rivière Niagara et le lac Ontario pour les métaux toxiques et surtout les substances organiques toxiques et 2) le réseau des rivières English et Wabigoon pour le mercure et le mercure méthylique. Pour l'examen préliminaire du transport et de l'enfouissement des contaminants dans ces réseaux, l'étude fait une description des progrès récents dans : 1) la spéciation des métaux toxiques dans les écosystèmes aquatiques; et 2) la sorption des substances chimiques organiques toxiques par les substances particulaires. Les données présentées ici sur la chimie en phases aqueuse et particulaire ont été obtenues en partie grâce à la mise au point et à l'utilisation sur le terrain de centrifugeuses à grande vitesse et d'extracteurs de liquide/substance aqueuse de grande capacité. Ces derniers ont permis de mieux évaluer l'importance de la phase aqueuse dans le transport des substances chimiques organiques toxiques. L'enfouissement des métaux et substances organiques toxiques est présenté ici en insistant sur : 1) la spéciation des métaux toxiques dans les sédiments de fond; 2) l'utilisation des carottes de sédiments datés pour illustrer l'évolution dans le temps des concentrations de contaminants organiques.

# Introduction

In 1978, I presented an earlier review of advances in sediment-related fluvial transmission of contaminants (Allan, 1979).[1] Most of the examples involved phosphorus in suspended loads or phosphorus forms in bottom sediments. Toxic metal data were rudimentary and dealt mainly with total metal concentrations in suspended loads and surficial bottom sediments. In spite of considerable information on distribution of total metals in sediment cores, the data often came from non-polluted locations. The information on toxic organic chemicals was mainly on concentrations in surficial bottom sediments. The conclusions from the review were that sediment was a major transport medium for phosphorus and probably toxic metals and possibly for hydrophobic toxic organics. I pointed out that a considerably expanded effort would be needed to resolve particulate/toxic metal and even more so particulate/organic contaminant interactions in aquatic ecosystems.

In the five years since 1978, information on metals in aquatic ecosystems has increased dramatically. There have been three international conferences on the subject of heavy metals in the environment. A book on *Metal Pollution in the Aquatic Environment* has been published (Förstner and Wittmann, 1981). Investigation of speciation of metals in bottom sediments from many locations in Europe has taken place. Since 1979, the Wabigoon-English River basin has become probably the most intensively studied large river-lake system in the world in terms of fate of one chemical (mercury) (Allan *et al*., 1984). Problems of organic chemical contamination in the Hudson River and the James River in the United States have been studied in some detail (Baker, 1980). In Canada, especially on the Laurentian Great Lakes, research into organic chemical fate has been extensively and intensively investigated. The prime Canadian site of toxic organic chemical research has been the Niagara River and Lake Ontario. A variety of chemicals and media have been examined (Allan *et al*., 1983).

The studies in Canada of toxic metal, organometal and organic chemicals have involved large outlays of capital on advanced analytical instruments and major expenditures of operational research funds. In this review, I will extract from this data base gathered in Canada on the Niagara River–Lake Ontario and English–Wabigoon River systems to discuss the state of the art with respect to our knowledge of the role of particulates in contaminant fate. I will also make use of examples from the literature, especially in terms of laboratory predictions of critical factors and processes.

The role of particulates in contaminant fate is virtually all-encompassing. Particulates are both abiotic and biotic. In size, they range from an arbitrary upper limit, which includes sand grains and zooplankton, to an arbitrary lower limit defined by filtering, centrifugation, or even precipitation of colloids. Particulates are an integral part of both geochemical and biological cycles of lakes and rivers. They are affected by and affect chemical, physical and biological processes. They are in intimate association with the aqueous phase. Particulates are influenced by and influence many contaminant fate processes. I have divided this large subject area into two parts.

In Part I, I will discuss

(a) The basic properties of particulates as they relate to an association with toxic metals and organic chemicals
(b) The basic properties of organic chemicals as they relate to an association with particulates
(c) The relative importance of particulates as toxic metal and organic contaminant transport media
(d) Burial of toxic metals and organic contaminants in aquatic system bottom sediments.

In Part II, I will discuss

(a) Direct chemical and biological methods of assessment of toxic organic chemical bioavailability
(b) Recycling of toxic organic contaminants by biological and physical processes
(c) Indirect assessment of bioavailability from analysis of bioaccumulation of hydrophobic, persistent organic contaminants in polluted aquatic ecosystems.

---

[1] The references for Part I are given at the end of the report.

Throughout the text, I will attempt to define our present knowledge and to make recommendations concerning what we need to learn. Some of these knowledge gaps only require more data acquisition, others involve trends, but many involve process research. It has been necessary to propose hypotheses, and these should be areas for testing by more extensive and intensive future research. For many toxic organic chemicals, there is undoubtedly much information on actual measurement and prediction of their fate. In other ways, however, we are still at the problem identification stage, and thus only now can start to predict accurately the aquatic fate of new organic chemicals in real aquatic ecosystems.

## SOURCES OF INFORMATION

In the last five years, the titles of several books, collections of papers or special journal publications have implied that there is a large published data base relevant to particulate-contaminant interactions. This is not the case. In fact, many of these volumes contain largely philosophical papers; repetitious reports or reviews by the same authors; or papers which rely heavily on discussion in the early stages and have only limited new data to report. All of these publications, of course, have some merit, and there are excellent papers scattered throughout these volumes.

One reason for the limited information available in the literature is the cost of conducting contaminant research, particularly on organic chemicals. Many environmental laboratories have moved from extensive nutrient research to limited heavy metal research, but only a few are able to invest the capital funds for new capillary gas chromatography; capillary gas chromatographic/mass spectrometry; high-pressure liquid chromatography; gas chromatographic/atomic absorption and other techniques needed to study organic and organometallic chemical fate. Also, the physical process of adequate sample collection may require that organizations have access to developmental engineering services that can build or modify bottom sediment coring devices; bottom sediment porewater peepers; field centrifuges; and liquid/liquid extractors. Much of the biological work relevant to contaminant fate is labour intensive. Large samples must be collected and laboriously physically separated prior to analysis. Examples are activities such as the separation of various benthic organisms for analyses or the analyses of fish stomach contents to trace food webs.

A second reason for the limited information may be that most contaminant data are not collected for hypothesis-testing research but rather for compliance monitoring purposes. Such information tends to be stored in large anonymous computer files and is seldom accessed unless water quality objectives or guidelines are violated. Much of this information may be of the trend analysis type and is often not publishable in journals. Part of this last problem is being addressed by new journals, which emphasize the importance of themes that interconnect information in a useful function rather than older journals, which tend to be discipline-oriented and where, for example, publications relevant to contaminant fate are rare items among large volumes of less problem-directed research.

A review of volumes of collected works from which information on the role of particulates in contaminant fate may be extracted shows that at least four of the recent best have been edited by Canadians on the shores of Lake Ontario, mainly at the Canada Centre for Inland Waters (CCIW). This is not too surprising because CCIW is the largest freshwater research institution in North America, and probably in the Western World. The Centre is also located in the Laurentian Great Lakes which comprise the world's largest single source of freshwater, but are a resource contaminated by a large number of toxic metals and organic chemicals. The Niagara River, which is only 50 km from the Centre, transports a wide range of toxic metals and over 400 organic chemicals, many of which remain as unidentified peaks on chromatograms. The four volumes are the following:

(1) MacKay, D., ed. 1982. *Physical Behaviour of PCBs in the Great Lakes*. Ann Arbor Science Pub. Inc., Ann Arbor, Mich., 442 pp.

(2) Leppard, G., ed. 1983. *Trace Element Speciation in Surface Waters and Its Ecological Implications*. Plenum Pub. Corp., 320 pp.

(3) Allan, R.J., A. Mudroch and M. Munawar, eds. 1983. The Niagara River-Lake Ontario Pollution Problem. Special Issue, J. Great Lakes Res. 9(2): 109-340.

(4) Nriagu, J. and M. Simmons, eds. 1984. *Toxic Contaminants in the Great Lakes*. Wiley and Sons, 550 pp.

Several papers, especially in (3) above, and to some extent in (4) and (1), deal directly or indirectly with the role of particulates in the fate of chemicals. The Lake Ontario volume (4) has 19 papers, of which six cover aspects of organic contaminants but none exclusively on particulate-contaminant interactions. The volume of 17 papers from the NATO Conference on Speciation of Metals (2) contains valuable information but only on toxic metals. The papers of most interest in relation to the topics discussed here are those by Batley (1983), Leppard (1983), Smies (1983) and Förstner and Salomons (1983b). Perusal of all of these publications provides the reader with a good overall impression of the total subject area of contaminants fate in freshwater systems and the relationship of this to limnological processes.

In addition to the above, there are four other important sources of information:

(1) Baker, R.A., ed. 1980. *Contaminants and Sediments*. Vol. 1. Fate and Transport, Case Studies, Modeling, Toxicity. Ann Arbor Science Pub. Inc., Michigan, 558 pp.

(2) Förstner, U. and G.T.W. Wittmann. 1981. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, 486 pp.

(3) Sly, P., ed. 1982. Sediment/Freshwater Interaction. Proc. of the 2nd Int. Symp., Kingston, Ontario. Hydrobiologia, 91/92, 700 pp.

(4) Golterman, H.L., P.G. Sly and R.L. Thomas. 1983. Study of the Relationship between Water Quality and Sediment Transport. Tech. Papers in Hydrology, No. 26, Unesco, 231 pp.

Of 26 papers in (1), there are three in which actual polluted sites have been studied in detail. Namely, several aquatic compartments have been analyzed for Kepone in the James River (Huggett *et al.*, 1980); for PCBs (polychlorinated biphenyls) in the Hudson River (Turk, 1980); and for PCBs in Lake Superior (Eisenreich *et al.*, 1980). This volume also contains three relevant papers on sediment toxicity tests referred to in Part II. Although the other papers in this collected work are important, they are limited in terms of transport, bioavailability and bioaccumulation of toxic chemicals. The second, (2) above, deals extensively with contaminated bottom sediments in rivers and lakes and emphasizes bioavailability of metals in bottom sediments as determined by chemical extraction techniques. The proceedings of the Sediment/Freshwater Interaction Conference comprises 68 papers, several of which concern toxic metals, but only one with organic chemicals (polynuclear aromatic hydrocarbons [PAHs]). Published early in 1984, (4) above devotes part of three of ten chapters to case histories of contaminant dispersion and burial.

There are now four Proceedings of the International Conferences on Heavy Metals in the Environment (Hutchinson, 1975; Perry, 1979; Ernst, 1981; and Müller, 1983). Whereas a data base exists on total heavy metal concentrations in various media, there are still only rare publications dealing with extensive multi-year, multi-media, heavy metal pathways and fate in aquatic ecosystems. Perhaps the most extensive and intensive study, certainly so in Canada, is the recently completed research study of mercury pathways and fate in the Wabigoon River system of northwestern Ontario (Allan *et al.*, 1984).

The importance of particulates in the fate of contaminants in aquatic ecosystems is gaining recognition, although even as recently as 1982 and 1983, papers on the topic were rare. Presentations of such papers are often made at large scientific meetings on broad topics or at best, in special symposia on specific pollution issues. The proceedings of such large gatherings usually include a wide range of science but only infrequently are data directly applicable to specific questions on contaminant fate.

However, 1983 saw some first attempts to arrange small meetings focused specifically on the important interface of particulates and contaminants. The International Joint Commission sponsored a workshop (in the true sense of limited attendance) in Bloomfield Hills, Michigan, for discussion of the "Transport and Fate of Particulate Associated Pollutants in the Great Lakes." This meeting was predominantly an internal review of work in the United States. It included atmospheric deposition of particulates, a subject open to considerable controversy with respect to sample devices and meaning of results, and a subject not discussed here. Presentations were made by leading U.S. researchers, to whose work I have referred here. The U.S. data base is strong in the laboratory areas of sorption measurements and kinetics, and in benthic mixing processes in polluted ecosystems. The Canadian data base on transport, burial and resuspension in the Niagara River and Lake Ontario is more extensive. Late in 1983, a special symposium on "The Role of Particulate Matter in the Fate of Contaminants in Aquatic Ecosystems" was held at the Chisholm Institute of Technology, Melbourne, Australia.

Early in 1984, the American Society of Oceanography and Limnology hosted a Special Symposium on "The Role of Particulates in the Fate of Pollutants in the Great Lakes" at their Annual Meeting held in New Orleans. Publication of some of the papers presented at this meeting will probably occur later in 1984 and beyond. An International Workshop on "The Effects of *In Situ* Contaminants" will be held in Aberystwyth, Wales in late 1984.

CHAPTER 2

# Overview of the Role of Particulates in Contaminant Fate

Particulate matter plays a critical role in the physical movement, chemical speciation and biological fate of both toxic metal and organic contaminants. Three media—water, sediment and biota—are significant in terms of pollutant transport. Water is usually the primary medium. Toxic metals and many of the more commonly detected toxic organic chemicals, however, are often closely associated with suspended particulates and bottom sediments, and this phase becomes more significant during events such as spring runoff or storms. Contaminants are usually more readily measurable in suspended particulates than in filtered water. Suspended loads have often been considered to be the major transport media for toxic metals, especially when the suspended load is high.

Bottom sediments are the primary contaminant sink in aquatic ecosystems. Bottom sediment resuspension and other processes such as direct uptake of bottom sediment contaminants by biota, bioturbation, and re-establishment of new equilibria with overlying water can extend the time period during which contaminants in bottom sediments remain bioavailable and thus bioaccumulate. The critical rates required to model the aquatic fate of toxic metals and hydrophobic organics include sedimentation rates, sediment resuspension rates, and sediment/water partitioning rates (and coefficients). Unfortunately, these rates are usually site specific because they depend on hydrodynamics, limnology and sediment quantity and type. Thus, knowledge of the specific limnology of each aquatic system can be as important as knowledge of specific chemical properties determined in controlled environments.

Suspended particulates have higher concentrations of contaminants and thus a greater bioavailable component, which translates into a greater potential for exposure than may occur from the aqueous phase. For smaller rivers, a higher percentage of the suspended load is usually transported in the spring runoff or immediately following major rainfall events. In Canada, suspended loads, generated by snowmelt/spring runoff, are usually highly mineral (residual) in composition. Because of this, the toxic metal particulate component transported in the spring often has a low bioavailable fraction. Hydrophobic organic contaminants transported on the sediment in the spring are, of course, not present in residual mineral forms, and the entire load may be potentially bioavailable. In summer months, the suspended loads, both abiotic and biotic, are often largely organic in composition and contain a higher bioavailable fraction. The composition of particulates influences the form or speciation in which a contaminant is transported, and in turn this influences bioavailability. Both biotic and abiotic particulates play a central role in the transport and fate of toxic metals and organic contaminants in aquatic ecosystems, as has long been appreciated in the interaction between plant protection materials and soils in agricultural research. A similar importance for particulates is becoming increasingly recognized in the aquatic sciences in terms of fate of toxic metal and organic contaminants.

In rivers, the particulate load is the most important factor controlling the partitioning of toxic contaminants between what is really in, or is operationally defined as being in, solution. In Canada, some rivers, such as the North Saskatchewan in the Prairie region, have high suspended particulate concentrations, whereas others, such as the Niagara River, have relatively low suspended particulate concentrations. Alternatively, the volume of suspended particulates transported in the latter greatly exceeds that of the former because of the great difference in mean annual flows. All of these variables must be considered when assessing the relative importance of particulate versus aqueous transport. Namely, interconnections between flow, particulate concentrations and chemical speciation or compartmentalization must be resolved if chemical transport and fate are to be understood and predicted. In lakes, the presence of suspended particulates of abiotic and biotic character depends on the following:

(a) The particulate load of rivers entering the lake

(b) The trophic level of the lake

(c) The sedimentation rates

(d) The predisposition of the lake to various types of resuspension processes or processes that maintain particulates in suspension.

When a river enters a lake, much of the chemical load is rapidly sedimented near the river inflow, often in submerged deltas. Sediment cores from such sites provide good historical records of changing toxic contaminant loads to the lake. Surficial bottom sediments taken throughout a lake can reveal the distribution of a chemical and its ultimate fate in major depositional basins. Sedimentation is not, however, the final influence of particulates on chemical fate. Particulate resuspension is extensive in many shallow and even very large lakes where it can result in a nepheloid layer.

For the Great Lakes, primarily Lakes Michigan, Erie and Superior, Eadie *et al.* (1983) prepared a status report on sorption and partitioning; particle transport and settling; early diagenetic processes in lake sediments; interactions on sediment; and contaminants and benthic organisms. All these subject areas involve relevant particulate toxic metal/organic interactions. The persistent organic compounds identified to date as the major problems in the Great Lakes are those that are highly partitioned onto suspended and bottom particulates. Chronologically, they have been DDT in the 1960s, PCBs in the early 1970s, mirex in the late 1970s, and PAHs, CBs and TCDDs in the early 1980s. All of these chemicals are subject to varying degrees of internal recycling by chemical, physical and biological processes. In the conceptual model developed by Eadie *et al.* (1983), particulates occur in three compartments (Fig. 1). Particulates are important in a large number of processes outlined by this model, namely 2, 4, 8, 10, 12, 13, 14 and 15. Eadie *et al.* (1983) listed hypotheses for testing these particulate-influenced processes. I have amended and reordered these hypotheses under the following four headings.

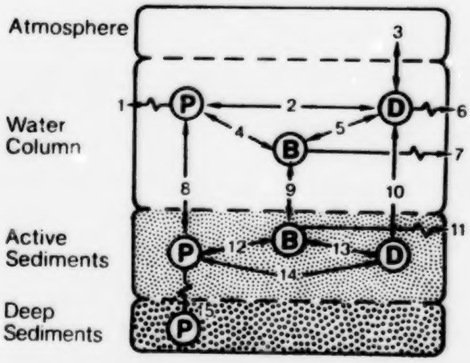

**Figure 1.** Conceptualized toxic system model. *P* – particle phase; *D* – dissolved phase; *B* – abbreviated food web. Process arrows are numbered: *1* and *6* (photolysis); *1* and *14* (sorption); *3* (air-water exchange); *4* (grazing and fecal pellet generation); *5* (filtering); *7* and *11* (biological decomposition); *8* (settling and resuspension); *9* (food-web dynamics); *10* (advective and diffuse mixing); *12* and *13* (benthos-sediment interactions); *15* (burial and bioturbation) (after Eadie *et al.*, 1983).

### (1) *Transport*

Partitioning of selected synthetic organic contaminants is proportional to compound solubility and can be represented as an equilibrium.

The equilibrium partition coefficient is inversely related to particulate concentration.

### (2) *Burial*

Particle residence times in the water column are less than one year.

Burial in deep sediments is a significant removal process for selected organic contaminants.

Fecal pellet settling is the primary removal mechanism from the water column for selected contaminants.

### (3) *Recycling*

The movement of particle-bound contaminants into sediment catchment basins is controlled by storms during the unstratified period.

The downslope movement of particle-bound contaminants is dominated by nepheloid layer processes.

Resuspension, during the stratified period, introduces significant amounts of contaminants into the epilimnion.

Resuspension, during the unstratified period, significantly increases contaminant half-lives in the water column.

Upwelling events introduce a significant amount of sediment-bound contaminants into the epilimnion.

Bioturbation of recent sediments, combined with resuspension, significantly increases the residence time of selected organic contaminants in the water column.

### (4) *Bioaccumulation*

Benthic organisms obtain a significant fraction of their body burden of selected organic contaminants directly from the sediment/pore water system.

A significant fraction of the body burden of top predator fish comes from benthic organisms.

Zooplankton, benthos and fish acquire more than 50% of their body burden of selected contaminants by adsorption through their gills.

Canadian and American scientists researching Great Lakes pollution problems are attempting to answer these and related questions. Much of the following information on the Niagara River/Lake Ontario pollution problem is aimed at the resolution of these hypotheses. Answers to these hypotheses can be attained from three related water quality activities, namely compliance monitoring, surveys and trend analyses, and hypothesis-testing research.

# Particulate Speciation of Toxic Contaminants

Suspended materials are complex mixtures of minerals and organic solids coated with Fe and Mn oxides and organic substances involved in sorption reactions with toxic metals and organics. Sorption of metals in aquatic ecosystems occurs on several substrates in a variety of ways (Förstner and Salomons, 1983b).

(1) *Physical sorption*

van der Waals forces.

Ion-dipole interactions.

Dipole-dipole interactions.

Occlusion in iron oxides, Al oxides, zeolites.

(2) *Chemical sorption*

Bonds between ions in solution and the surface of particulates.

Condensation reactions with OH groups on the surface of Si, Fe, Mn, Al compounds.

(3) *Ion exchange*

Negative or positive charged lattice compensation by negative or positive ions from solution.

(4) *Sorption on Fe/Mn oxyhydrates*

By isomorphous substitution.

Amorphous conglomerates.

"Aged" coatings.

(5) *Sorption on organics*

Algae, bacteria reactions.

Decomposed biotic material.

High molecular weight colloids.

Lower molecular weight sorption coatings on clay or metal oxyhydrate substrates.

Although laboratory studies have determined surface complex formation constants for specific media, sorption processes in the field are usually much more complex interactions involving a range of processes with generic names such as adsorption, flocculation, polymerization and precipitation. The last occurs by oxidation or reduction, in the following forms: sulphides, carbonates, sulphates, oxides, and hydroxides.

The role of inorganic and organic particulates in the distribution of contaminants between dissolved and solid phases is primarily important because particulates offer sites for sorption. A prime medium for sorption by sediments is metastable iron and manganese oxyhydrates which have a high degree of isomorphic substitution. Some metals such as Cu, Co, Ni and Zn tend to associate with Mn. Others such as arsenic tend to associate with Fe, at least in Fe/Mn nodules. A second major sorption medium consists of organic material, which in aquatic systems mostly has the characteristics of fulvic acid. The sorption capacity of such natural organics usually lies between that of clay minerals and metal oxyhydrates. Formation of metal/organic complexes in solution may enhance adsorption if the organic ligands are adsorbed onto mineral surfaces. On the other hand, it may prevent adsorption if the complexing ligands form strong metal/ligand complexes which are not adsorbed onto mineral surfaces. In the solid phase, speciation of metals is mainly determined by the nature of particulate surfaces. The surfaces of particles are often covered with hydrous iron and manganese oxides and/or organic films of presently unknown, or only speculated, composition but with a great ability to remove toxic metal and organics from solution. Aging effects and other diagenetic processes that take place after deposition of particulates can cause redistribution of toxic metals and organics between the various components of bottom sediments and overlying water. The usual result is a stronger binding to the particle phase.

Sediments are a substrate for biogeochemical transformation processes resulting in the formation of methylated species of some trace metals such as mercury. Methylated forms are recycled to the pore waters and to the water column where they may further indirectly influence the speciation of dissolved metals. Diagenetic changes in bottom sediments can also enrich dissolved organic matter in interstitial waters and may influence the speciation of the interstitial trace metals. Physical, chemical or biological processes may release these re-speciation metals to overlying waters where they may again influence the speciation of metals there. Ultimate speciation of a metal in an aquatic ecosystem is difficult to predict because of the competition between the inorganic/organic phases in both the "soluble" and "particulate" fractions. Förstner and Salomons (1983b) have represented this complex, competitive situation in schematic form (Fig. 2).

Lee (1975) stated that three main criteria are relevant to the fate of toxic metals associated with particulates:

(1) *Time*
There is greater incorporation of contaminants into particulates with time.

(2) *Age of precipitates*
The older the hydroxide precipitate, the less the sorption capacity.

(3) *Natural organics*
Iron and its associated metals can combine with natural organic matter to form organometal colloids.

Förstner and Salomons (1983b) reviewed ways by which particulates interact with heavy metals. In water, there is usually reduced sorption of metals when strong organic chelators are present. Thus the "dissolved" organic complexing capacity of waters has implications with respect to surface water metal transport, burial and bioavailability. Maximum sorption of Cu by organic ligands occurs at higher pH values. Thus, increased acidity results in a decrease in Cu-ligand sorption by solids because of competition between the ligand and the Cu-ligand complex for surface sites. Alternatively, if the organic ligands themselves are sorbed to iron oxide coatings on particles, this may increase the metal sorption capability of the particulate coatings. In general, if sorption of the organic/inorganic particulate phase increases with a rise in pH, then the ligands are considered "ligand-like," but if it decreases they are considered "metal-like." Experimental results such as lowering of pH to cause rapid removal of Pb and Cd previously sorbed into salt marsh sediment (Fig. 3) are related to such metal/organic-particulate interactions.

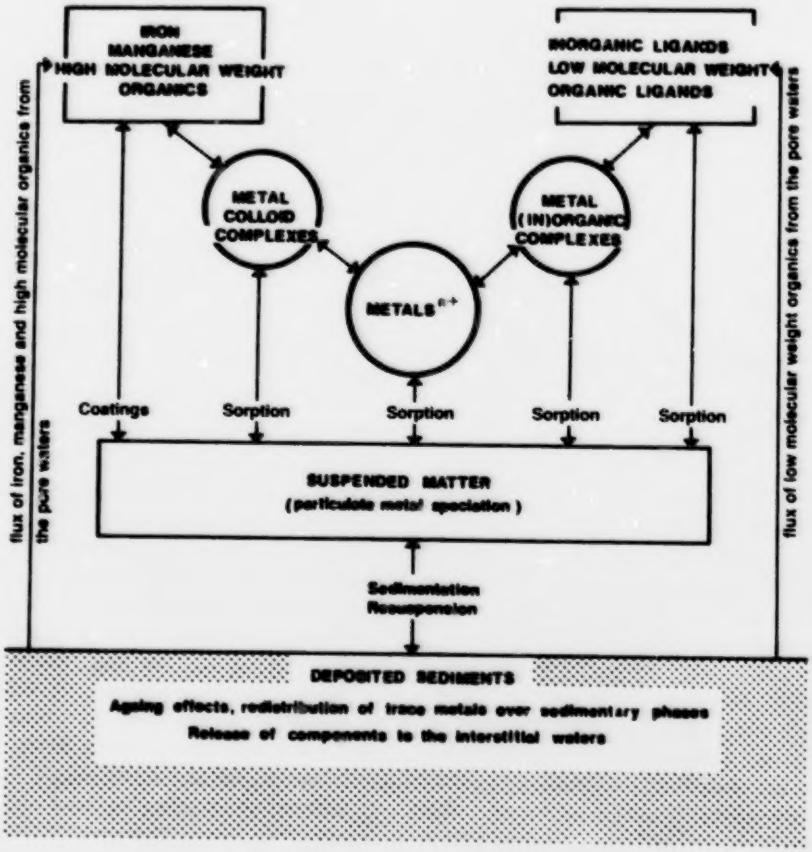
IRON
MANGANESE
HIGH MOLECULAR WEIGHT
ORGANICS
INORGANIC LIGANDS
LOW MOLECULAR WEIGHT
ORGANIC LIGANDS
flux of iron, manganese and high molecular organics from the pore waters
METAL COLLOID COMPLEXES
METAL (IN)ORGANIC COMPLEXES
METALS$^{n+}$
flux of low molecular weight organics from the pore waters
Coatings
Sorption
Sorption
Sorption
Sorption
SUSPENDED MATTER
(particulate metal speciation)
Sedimentation
Resuspension
DEPOSITED SEDIMENTS
Ageing effects, redistribution of trace metals over sedimentary phases
Release of components to the interstitial waters

Figure 2 Summary of major processes and interactions between dissolved and particulate metal species in surface waters (after Förstner and Salomons, 1983b).

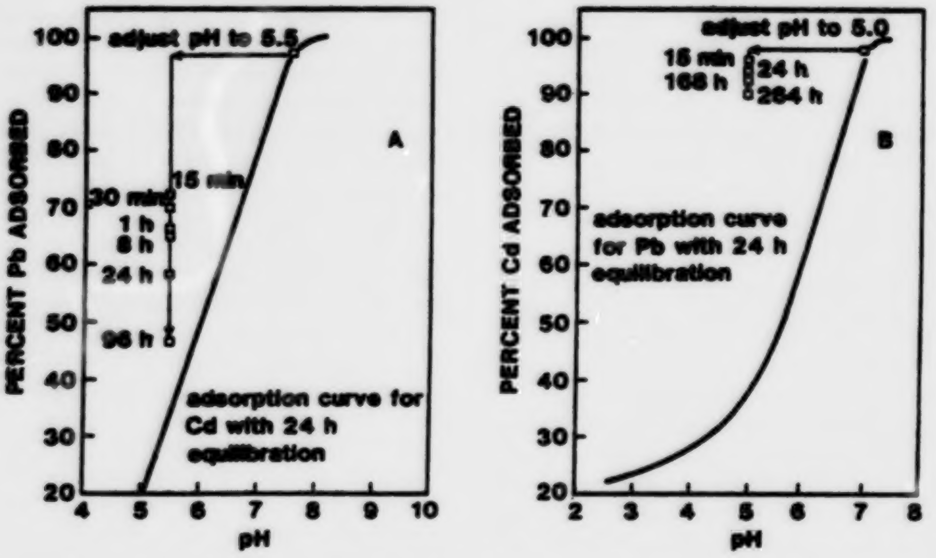

Figure 3. Kinetics of desorption from unaltered salt marsh sediment: *A* – lead; *B* – cadmium (after Salomons and Förstner, 1984).

In marine situations, most metal hydroxides and carbonates do not precipitate because of low concentrations. Instead, scavenging of metals by solid surfaces is seen as the main process of removal from the water column. Particles immersed in seawater rapidly lose the surface characteristics that they exhibit in pure solutions and acquire weakly electronegative properties, which imply the coating of surfaces by macromolecular organic films. The same process may increase surface complexing capacity of particulates in freshwater environments. The effect of coatings has been suggested as the reason why the sorption capacity of "clean" clay was less than that of clay sediment from lake beds (Rudd *et al*., 1984). In artificial enclosures in lakes, the latter was shown to have a greater capacity to remove added Hg from solution. Thus sorption models based on pure solids are not a particularly helpful avenue of research because pure solids are rare in nature.

The various organic and inorganic phases of particulates are closely interrelated because clay minerals, carbonates and other suspended materials are sites for deposition of Fe and Mn hydroxides, which are then sites for organic surface coatings. When systems are rich in natural organics such as humic and fulvic acids, the role of Fe and Mn oxides as direct sorbers of metals may be overshadowed by humic-fulvic/clay complexes. Organic-metal complexation may enhance partitioning to particulate matter if the metal-organic complexes formed are able to absorb better to particulate surfaces than the metal alone. Organics may themselves partition onto particulates and then form complexes with metals in solution, thus partitioning these metals into the particulate phase. The coarser biotic material (plankton) in the particulate form is usually larger than 0.45 $\mu$m and is separated by routine filtration or centrifugation. The smallest particle size, organic material in water, is present as colloids and may complex with metals or sorb dissolved organic chemicals. Colloids pass through high-speed centrifuge systems. Bottom sediments usually contain varying degrees of colloidal organic material, which can be important for partitioning of metals and organic chemicals between sediments, pore water and overlying waters.

Organic coatings on particulates could arise from bacterial or algae excretions, breakdown of plant and animal material, and absorption of low molecular weight colloids. Weak organic acids, compounds with phenolic and carboxylic groups, and natural organic matter have all been shown to bind to oxide surfaces. Sorption is at a maximum around pH 5 and decreases with increasing pH. Especially for organic chemicals, as will be discussed later, the relationship of $K_d$ (or $K_{oc}$) to $K_{ow}$ implies that organic matter, perhaps in many cases as presently unmeasured organic surface coatings on particulates, is intimately involved with the partitioning of hydrophobic organics onto particulates. The analyses of these suspected organic coatings and their role in contaminant partitioning require investigation of a more fundamental nature than can be conducted by presently available selective chemical extraction techniques. Evidence for the homogeneity of surface coatings of particles has come from electrophoresis measurements (Hart, 1982), which demonstrated that for 80 particles from the Yarra River, all had a negative surface charge and there was only a slight variability in mobility with particle type (Fig. 4).

Strength of sorption increases with time, a well-known fact from soil nutrient and trace metal bioavailability research. Non-easily reversible sorption of metals also occurs with aquatic sediments. Salomons and Förstner (1984) added Cd and Zn to freshwater suspended material, permitted sorption to occur for 1 to 60 days, extracted the metals with NaCl at 19% of seawater composition, and found that the less metal removed, the longer the sorption period (Table 1). The same type of experiment over a seven-month sorption period with Mediterranean sediment showed that Cd would be 100% removed by an acetic acid/ammonium acetate (pH 5.4) extractant. For Pb, Zn, Cu and Co, the corresponding values were 50%, 4% to 33%, 0%, and 33%, respectively. Other results of the same type are reviewed by Förstner and Salomons (1983a).

**Table 1. Percentage of Cadmium and Zinc Not Released from Suspended Matter in River Water after Treatment with NaCl**

| Metal | Adsorption time (days) | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 8 | 24 | 60 |
| Cadmium (%) | 24 | 30 | 33 | 37 | 40 |
| Zinc (%) | 60 | 67 | 70 | 74 | 88 |

After Salomons and Förstner (1984).

Sequential extraction techniques (SET) can be used to separate trace metals into transport and deposition phases. In agricultural research, SET were developed in the early 1950s to measure soil bioavailable nutrient components. However, trace metals in soils were seldom examined by SET. Instead, one chemical, usually a dilute acid, was used to extract the total bioavailable trace metal content. The common extractants were citrate-bicarbonate-dithionite (CBD); acetic acid; hydroxylamine hydrochloride; ethylenediamine-tetraacetic acid (EDTA); and oxalic acid-hydroxylamine. In the late 1970s and early 1980s, procedures for sequential extraction of trace metal components in aquatic sediments were developed (Tessier *et al.*, 1979; Salomons and Förstner, 1984). Sequential extraction techniques can be used as a means of estimating strength of sorption or bonding. Phases separated by SET are never absolute because of the effects of solution to solid ratio, the original

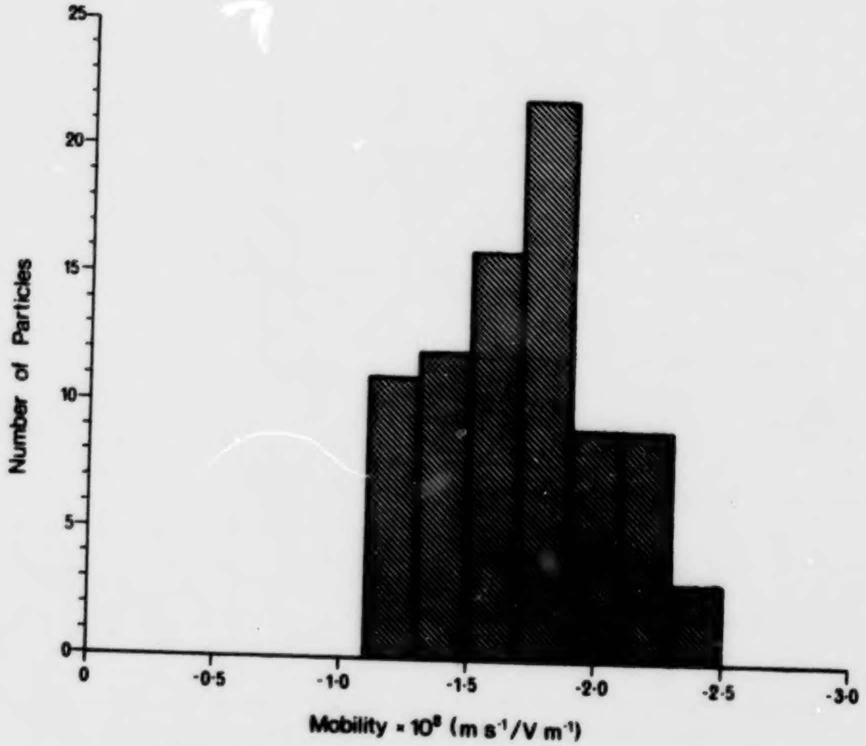

**Figure 4.** Electrophoretic mobility of Yarra River particles (after Hart, 1982).

chemical status of the sediment, and the efficiency in dissolution. Different extractants used or proposed by different individuals are expected to remove particulate-associated trace metals (Salomons and Förstner, 1984) held in different phases as follows.

| Phase | Extractants |
|---|---|
| Adsorbed and cation exchange | $BaCl_2$ – triethanolamine, pH 8.1<br>$MgCl_2$<br>Ammonium acetate, pH 7 |
| Carbonate | $CO_2$ – treatment of suspension<br>Acidic cation exchanger<br>NaOAc/HOAc – buffer, pH 5 |
| Reducible* | Acidified hydroxylamine (+ 0.01 *M* $HNO_3$)<br>Ammonium oxalate buffer<br>Hydroxylamine-acetic acid<br>Dithionite-citrate buffer |
| Organic† | $H_2O_2$ – $NH_4OAc$ (pH 2.5)<br>$H_2O_2$ – $HNO_3$ |

*In approximate order of release of iron.
†Including sulphides.

Only in the late 1970s, when soil chemical SET methods were extended to aquatic sediments, were different extractants experimented with so that the different phases extracted were pertinent to aquatic ecosystems, both freshwater and marine. Many toxic metals occur naturally and separation of the natural from the anthropogenic component was essential (Allan, 1975). The forms (or species) extracted led to the use of the term "speciation." Chemical estimates of speciation are usually aimed at estimates of bioavailability but also provide useful information on modes of contaminant transport and burial. Salomons and Förstner (1984) proposed a simple four-step extraction with the following:

(1) *Acidified hydroxylamine hydrochloride at pH 2*
Extracts exchangeable cations and carbonate-bound metals.

(2) *Acidified hydrogen peroxide*
Removes the organic fraction.

(3) *Ammonium acetate*
Removes any metal ions reabsorbed during the $H_2O_2$ extraction.

(4) *Total analysis with hydrogen fluoride and perchloric acid*
Removes the residue remaining after the three extractions above.

All sequential extraction technique procedures are an ongoing subject of much debate and occupy several researchers worldwide. For example, past use of $H_2O_2$ may have solubilized Fe and Mn oxides, thus overestimating the content of metals in organic fractions. Pfeiffer *et al.* (1982) tested a three-stage extraction sequence with buffered hydroxylamine hydrochloride (pH 2), oxalate or dithionite solutions, to differentiate the reducible phase of heavy metals in marine sediments. The buffered oxalate gave the best estimate of the authigenic heavy metal fraction. Dithionite was abandoned for reasons described by Tessier *et al.* (1979). The hydroxylamine-hydrochloride solution is now considered to be particularly valuable in terms of measuring recycling of metals by chemical release of metals (Calmano and Förstner, 1983).

The sequential extraction technique is usually applied to separate the exchangeable, the easily reducible, the moderately reducible, the organic, and the residual fractions in particulates. Changing chemical conditions usually release metals from the first two fractions, but biological processes may release them from all but the last. For San Francisco Bay sediment, 50% of the Cd and Cu was present in organic phases, whereas 70% of the total Pb was associated with Fe/Mn oxides. This technique resolved the processes of transport of these metals on particulates, and the changes in phase with sedimentation, burial and diagenesis. Another use of SET is to obtain sorption isotherms from the already extracted sediments. These isotherms provide valuable insight into the resolution of the particulate phase responsible for metal sorption. Lion *et al.* (1982) used this technique to determine the component responsible for Cd sorption by salt marsh sediment. The percent of metal absorbed at the same pH declined after the organic content of the sediment was removed (Fig. 5), thus implicating the organic phase as being responsible for Cd sorption.

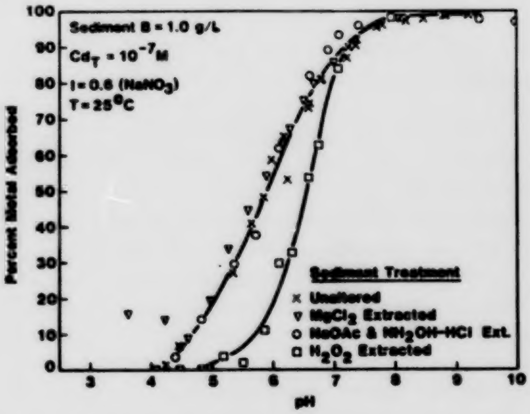

**Figure 5.** Cadmium adsorption onto sequentially extracted estuarine salt marsh sediment (after Salomons and Förstner, 1984).

Different species of metals have different biological effects. Arsenic occurs as both inorganic and organic forms. Cadmium is strongly complexed by organics, as is copper. Complexation of Cu, mostly by the fulvic acids, may reduce its toxicity. Inorganic Hg may be rendered biologically unavailable by complexation with humic acids or sorption to particulates. However, methyl-Hg is highly toxic. Overall, there is a need to relate more effectively metal speciation and bioavailability, as determined chemically, to biological estimates of toxicity. Few publications deal with this topic except as it applies to phytoplankton (Smies, 1983). The same deficiency exists for assessing *in situ* biological effects of organic contaminants. The SET techniques can be used to assess bioavailability and, in turn, this permits conclusions to be drawn on real exposure and hence toxicity can be predicted. Biota can alter metal species themselves by excretion of a metal in a more toxic form than that in which it was taken up.

In summary, clay minerals, clay-rich aggregates and heavy minerals are the major carriers of toxic metals in suspended loads, but the major accumulative phases in specific environments are Fe/Mn oxides, carbonates and sulphides. The sequential extraction technique can be used to analyze suspended loads to see how metals are transported. Anthropogenic metals introduced into aquatic systems are usually present in the exchangeable and easily reducible fractions of both suspended and bottom particulates. In particular, bottom sediments can be analyzed by SET to show pollution sources and the degree to which toxic metals are accumulated and eventually buried in aquatic ecosystems.

# Particulate Sorption of Toxic Organic Contaminants

In natural waters, the fate of hydrophobic organic chemicals, those compounds with a low (less than a few parts per million) solubility, is highly dependent on their sorption to suspended particulates. Sorption is a key process involved in the physical transport of toxic organic contaminants and in their degree of bioavailability and eventual bioaccumulation (as discussed in Part II). Because particulates reduce the pollutant concentration "in solution," they buffer the immediately and directly bioavailable aqueous phase contaminant concentration. In the field of soil science, the large number of chemical and physical parameters and solvent (water)/sediment properties affecting sorption have been researched for decades. Concentration of competing chemicals in the water, sediment type, and a host of other factors would seem to preclude a simple systematic procedure for predicting sorption characteristics of aquatic sediment.

Karickhoff *et al.* (1979) were the first to develop a predictor of partitioning of organic chemicals between water and aquatic sediments. Their research at the United States Environmental Research Laboratory, EPA, Athens, Georgia, was built on earlier research in soil science, where sorption as a cause of low pesticide efficiency had been studied for many years. In the soils field, the role of organic matter had been related clearly to properties similar to those of an organic solvent (Lambert, 1967). Different chemicals have unique and distinct sorption isotherms for different sediments. However, given a specific concentration of the chemical in water and a specific concentration of suspended sediment, a specific partition coefficient ($K_d$) can be measured. This $K_d$ is characteristic of both the chemical and of the sediment.

The first and most important characteristic affecting $K_d$ is the *concentration of the chemical in solution*. The $K_d$ is measured as an equilibrium constant between the concentration of contaminant in the particulate phase and the concentration in solution, i.e., at a given sediment concentration, the concentration of the chemical in solution controls the amount sorbed (Fig. 6). This is only true at relatively low sediment concentrations of up to 20 mg/L.

The second controlling factor is *suspended particulate concentration*. Connor and Connolly (1980) showed that there is an inverse relationship between concentration of absorbing solids and partition coefficient (the ratio of the

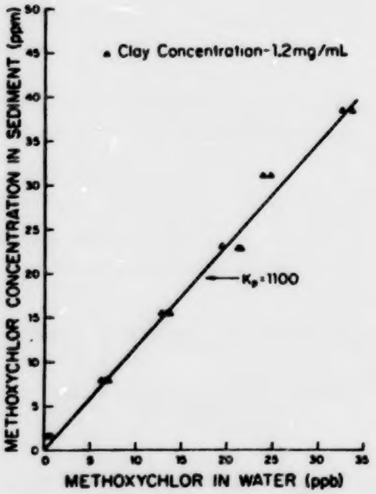

**Figure 6. Adsorption isotherm for methoxychlor on Hickory Hill clay (after Karickhoff *et al.*, 1979).**

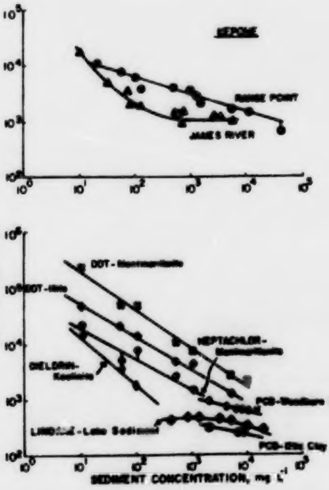

**Figure 7. Partition coefficient as a function of the concentration of particulates and particulate type (after Connor and Connolly, 1980).**

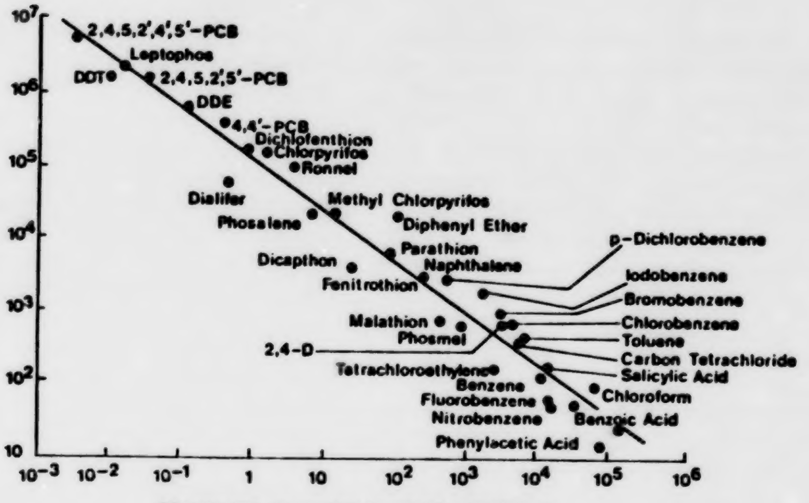

Figure 8. Relationship of $K_{ow}$ to water solubility (after Chiou *et al.*, 1977).

solid phase concentration to the dissolved phase concentration in the linear portion of the Langmuir sorption isotherm) (Fig. 7). Using Range Point sediment, a change in sediment concentration from 100 mg/L to 1000 mg/L lowered the partition coefficient for Kepone from 5900 to 3400. Above sediment concentrations of 20 mg/L, the sorption relationship is no longer linear and progressively less of the chemical becomes absorbed, i.e., the $K_d$ decreases.

The third controlling factor is *particulate type*. The differences between DDT sorption on illite versus montmorillonite, and Kepone sorption on James River sediment versus Range Point Marsh sediment, are shown in Figure 7.

The fourth important sediment parameter controlling partitioning sorption is *natural organic content* of particulates. Suspended particulates in aquatic systems can, in fact, be entirely organic, namely zooplankton, phytoplankton and bacteria. Centrifugation of this material results in a dark organic paste, which by virtue of bioaccumulation and sorption can contain high concentrations of toxic organic chemicals and metals. Other suspended particulates, especially resuspended bottom sediments in the Great Lakes, are made up primarily of inorganic material, and usually have an organic carbon content of some 3%. The organic content can rise to 30% in many lakes in the Canadian Shield where gyttja is the dominant lake sediment type. As mentioned earlier, when low percentages of organic matter are present, some of this may be in the form of thin coatings on mineral substrates. Removal of toxic organic chemicals from solution and their partitioning onto particulates may not be so much of a sorption process as one of exclusion and solubilization of the organic chemical into an organic (lipid-like) surface layer on particulates. As water solubility increases, the octanol/water partition coefficient ($K_{ow}$) for a toxic organic chemical decreases (Fig. 8) or the compound becomes less soluble in lipid-like organic media. Thus carbon (OC) content (or the quantity of organic coating) of the suspended and bottom particulates is critical to the degree of partitioning. The partitioning of methoxychlor was linearly related to organic carbon content of sediment (Fig. 9). Karickhoff *et al*. (1979) defined sediment $K_d$ as equal to $K_{ow}$/OC, where OC is a fractional content of organic carbon in a sediment. Thus $K_d$ can theoretically be predicted from the $K_{ow}$ for the chemical and the organic carbon content of a sediment.

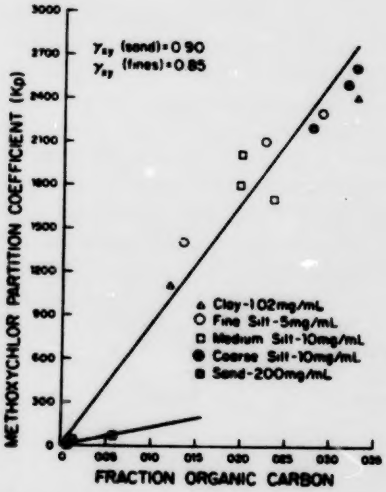

Figure 9. Methoxychlor $K_p$ as a function of particulate organic carbon content (after Karickhoff *et al.*, 1979).

Lastly, *time* affects sorption of toxic organic chemicals in that some 60% of total sorption is usually complete in two to five minutes. Equilibrium is established extremely rapidly in relation to the time required for environmental contamination and media sampling. There are, however, two components to the sorption phase, as has been known for many years from soil research:

(1) The rapid component completed in a very short time period and

(2) A slower component that often occurs only after a period of minutes but can continue for weeks or longer.

Conventional $K_d$'s, as determined in laboratories, are primarily a measurement of the rapid component. In the field, however, where exposure times can be very long, the slower sorption component may be important. When sediment contaminants are desorbed, it is usually only the rapid component that becomes quickly bioavailable. However, with time, the slower component eventually may also be released in real aquatic ecosystems, even when the extractant is only water.

There are large discrepancies for measured $K_{OW}$'s, often of several orders of magnitude, especially if the $K_{OW}$ is greater than $10^4$. The reasons are experimental and related to difficulties with solubilizing highly insoluble organic compounds; volatilization; contamination of the water phase with octanol; and chemical impurities.

As mentioned above, Karickhoff *et al.* (1979) had found that sorption was related to organic content of the sediments ($K_{OC} = 0.63\ K_{OW}$). Brown and Flagg (1981) showed that this relationship also held for nine chloro-s-triazine and dinitroaniline compounds. They included data from Karickhoff *et al.* (1979) and derived the relationship shown in Figure 10, namely:

$$\log K_{OC} = 0.937 \log K_{OW} - 0.006\ (r^2 = 0.95)$$

Table 2. Comparison of Estimated and Measured $K_{OC}$

| Compound | Measured data (literature) | | Estimated log $K_{OC}$ | | |
|---|---|---|---|---|---|
| | Log $K_{OW}$ | Log $K_{OC}$ | From $K_{OW}$ | From $X_{sol}$, mp | From $X_{sol}$ |
| γ-BHC (lindane) | 3.72 | 3.30 | 3.33 | 3.60 | 3.57 |
| α-BHC | 3.80 | 3.30 | 3.41 | 3.17 | 4.50 |
| 1,2-Dichlorobenzene | 3.39 | 2.54 | 3.00 | 2.96 | 2.62 |
| p,p'-DDT | 6.19 | 5.38 | 5.80 | 6.81 | 5.62 |
| 22', 44', 66'-PCB | 6.34 | 6.08 | 5.95 | 7.28 | 5.95 |
| 22', 44', 55'-PCB | 6.72 | 5.62 | 6.43 | 6.42 | 5.33 |

After Karickhoff (1981).

Table 3. Estimated Range of Sediment/Water Partition Coefficients for Various Pesticide Classes

| Pesticide type[1] | K | Characteristics of adsorption (sediments) |
|---|---|---|
| Organochlorines | | |
| Aromatic | $10^5$–$10^3$ | Few polar moieties; hydrophobic and van der Waals interaction; induction effects (polar substituents, non-conjugated double bonds) |
| Aliphatic | | |
| Organophosphates | | |
| Aliphatic derivatives | $5 \times 10^2$–$10^1$ | Active polar moieties (electron-rich heteroatoms, acidic hydrogens, heterocyclic nitrogen) |
| Phenyl derivatives | $10^3$–$10^2$ | |
| Heterocyclic | $5 \times 10^2$–50 | |
| Carbamates | | |
| Methyl carbamates | $5 \times 10^2$–2 | Highly polar; enhanced solubility; reduced adsorption vs organochlorines |
| Thiocarbamates | $5 \times 10^2$–50 | |
| Nitroanilines | $1 \times 10^3$–50 | Nonconjugated polar groups (contribute to electrostatic interactions); large molecules; strong hydrophobic forces |
| Triazines | 8–1 | Solar ionizable groups (amino-hydrogens); hydrogen bonding with water, low adsorption on soils |

[1] Total number of compounds examined: 160.

After Pavlou and Dexter (1980).

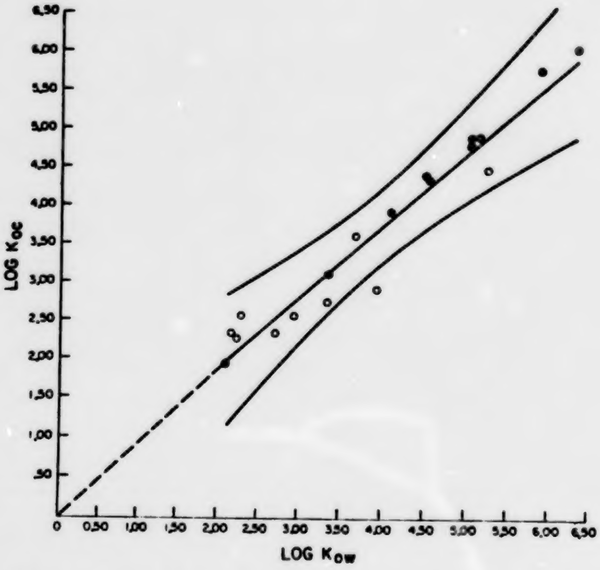

**Figure 10.** **Relationship between log $K_{oc}$ and log $K_{ow}$ for Hickory Hill coarse silt (Brown and Flagg, 1981).**

Karickhoff (1981) then reported that partition coefficients normalized to organic carbon content of sediments ($K_{oc}$ = $K_p$/fraction of organic carbon) were highly invariant over a wide range of sediment types. The equations developed to predict $K_{oc}$'s did so generally within a factor of two (Table 2). The equations were based on measured $K_{ow}$'s or on water solubility of the organic chemicals. Although much of the above is built on earlier studies of pesticide sorption in soils, the soils literature usually involves higher contaminant concentrations and organic matter content than found in aquatic ecosystems, and Karickhoff's results have provided a new and very valuable basis for predicting toxic organic chemical partitioning in aquatic ecosystems. In summary:

$$K_{oc} = 0.411\ K_{ow}$$

$$K_p = K_{oc} \times \text{fraction of organic carbon (OC)}$$

or

$$K_p = 0.411 \times K_{ow} \times \text{fraction of OC in the sediment}$$

Pavlou and Dexter (1980) summarized partition coefficients for classes of organic pollutants that occur in aquatic ecosystems. The range from high to low $K_p$ follows a shift from non-polar to semi-polar to polar characteristics, which primarily results in changes in water solubility (Table 3).

For hydrophobic organic chemicals with $K_d$'s of $10^5$, in rivers with suspended particulate concentrations of around 10 mg/L (which is just above that of the Niagara River), calculation shows that some 50% of the chemical will be in the particulate phase. If the suspended particulate concentration rises to 100 mg/L, as occurs in many rivers during high flow periods, then some 90% of the mass of contaminant could be in the particulate phase (Olsen *et al.*, 1982). There are many rivers (and lakes) throughout the world where suspended particulate loads exceed even 100 mg/L during specific event-related periods.

As noted earlier, charged pollutants such as metals will tend to associate with particulates by hydrogen bonding or ion-dipole interactions. For non-polar substances, such as some organic chemicals, an affinity for positioning at a water phase boundary is more important. Parks (1975) referred to this as hydrophobic bonding. If slightly polar, the organic pollutant molecule will orient itself so that the hydrophobic functional groups are away from the water phase and the polarized structure is directed toward the water. In waters, however, organic pollutants also become associated with or incorporated into other organic particulate phases both biotic and abiotic, including organic colloids.

In summary, the main factors affecting partitioning of toxic organic chemicals onto particulates in aquatic ecosystems are the same as those extensively studied by soil scientists. In order of importance, they are solubility of the chemical; concentration of the chemical; concentration of the sediment; type of sediment, particularly organic content or degree of lipid layering; time (reversible versus relatively irreversible); concentration of other chemicals and ions in solution; and temperature. Of these factors, only the initial properties of the chemical are defined. All of the others are site-related and influenced by various limnological processes. Thus, although laboratory tests do provide some basic understanding which can help to predict aquatic fate, real fate is usually site specific, and any chemical control or amelioration action at any specific site should be taken only after extensive site investigations.

# Role of Particulates in Transport of Toxic Metals and Organics

Suspended particulates and bottom sediments are commonly used as media to detect toxic metal and organic chemical pollution because concentrations are often in the parts per million or parts per billion range, respectively. In the aqueous phase, concentrations of toxic metals and organics are often in the low parts per trillion or even the parts per quadrillion range, respectively, and are thus difficult to measure with certainty. Suspended particulates may absorb much of the anthropogenic chemical inputs from point sources. Procedures used to trace pollutant pathways and fate usually involve study of

(a) One-point source situations
(b) Ratios of contaminants to each other or to a natural component
(c) Unique organic chemicals or radionuclides of unique source and loading history
(d) Use of radiotracers.

Predicting the fate of pollutants associated with fine-grained particulates is more difficult than when the chemicals are in solution. The dynamics of small particles are governed by the physical, chemical and biological processes that affect the fate of the particulates themselves (Olsen *et al.*, 1982) and thus their associated pollutant load. Once a pollutant has become associated with a particulate, its fate during transport is influenced by

(a) Sorption/desorption
(b) Flocculation
(c) Precipitation and coprecipitation
(d) Degradation and transformations
(e) Bioaccumulation
(f) Short-term events (floods, high wind stress)
(g) Sedimentation rates
(h) Resuspension episodes
(i) Pore water release
(j) Burial.

During burial in bottom sediments, the processes involved include

(a) Accumulation
(b) Mixing
(c) Mineralization.

Transfer rates associated with all of the above processes require better understanding.

In rivers such as the Mississippi, Yukon and Amazon where suspended loads are high, 90% of the total Co, Cu, Zn, Cr and Ni loads is transported in the particulate phase. Usually the bulk of the total metal load is in the lattice of minerals (Presley *et al.*, 1980) or is residual by SET. When total metal contents of suspended sediments in rivers are determined, the total loads transported by this medium can be very large. Förstner and Salomons (1983b) (Fig. 11) have provided data for some of the rivers of northwestern Europe.

Hydrophobic organic compounds introduced into aquatic ecosystems are also dispersed and accumulated primarily under the influence of particle dynamics. In the Hudson River, the bulk transport of PCBs to the ocean is during spring runoff and storm events associated with high suspended particulate concentrations (Bopp *et al.*, 1981). The total concentration of a hydrophobic chemical being transported in a river system can be a direct reflection of the quantity of suspended load. Feltz (1980) shows this relationship for total PCBs in the Hudson River from data collected by Turk (1980) (Fig. 12). In some rivers, biological productivity during higher temperature periods becomes the critical factor affecting particulate-dominated transport of contaminants. In the James River, which flows through Richmond, Virginia, to Chesapeake Bay, the highest concentrations of PCBs, DDT and Kepone on suspended particulates occurred in the low-flow summer months as a result of increased partitioning to suspended organic particulates (Huggett and Bender, 1980) owing to increased primary productivity in the warmer summer months. Huggett *et al.* (1980) measured concentrations of 20 to 200 ppm of Kepone in suspended particulates in the

James River. Kepone concentrations in river bottom sediments were up to 190 ppb; in phytoplankton, 1.3 ppm; in zooplankton, 4.8 ppm; and in various fish, from 0.08 to 2.7 ppm. White perch muscle contained up to 10 ppm Kepone. As expected, the Kepone maximum in bottom sediments occurred at the transition from fresh to salt water primarily owing to higher sedimentation in this zone. Near the original source of the Kepone, concentrations were highest in coarse bottom sediments of 63-μm size. In the lower estuary, maximum bottom sediment concentrations were in the particles <3.9 μm in size and were associated with high carbon content. The sediment water partition coefficient for Kepone is around $6 \times 10^4$. Using this partition coefficient, water concentrations may be predicted to be around 45 ppt. Organic content of the sediment is obviously important in terms of partitioning of the Kepone, and clearly Kepone bioaccumulates. The highest concentrations of Kepone are not at the top of the food chain, an environmental distribution which also occurs with other highly hydrophobic and highly toxic contaminants in other aquatic ecosystems.

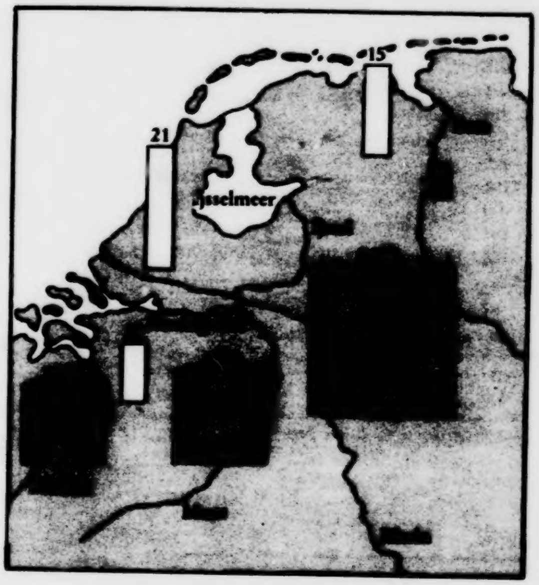

Figure 11. Yearly transport in tons of metals in the suspended particulates of rivers in northwestern Europe. Solid blocks – suspended sediment load in tons; open blocks – amount of bottom sediment dredged (after Förstner and Salomons, 1983b).

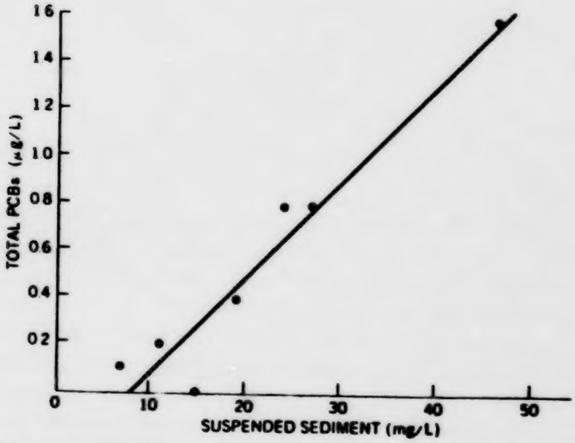

Figure 12. Relationship of total PCBs to suspended particulates in the Hudson River at Schuylerville, New York, April 1977 (after Feltz, 1980).

The relative proportion of contaminants in "water" versus suspended particulates requires consideration in any contaminant fate study. Although the concentrations in the suspended material may be high, the proportion in this medium, even for very hydrophobic compounds, can be low. For example, in Lake Superior, Eisenreich *et al*. (1980) found PCB concentrations in the surface floc at the lake bottom to be some 130 ppb. Assuming that this is the concentration of settling particulates, and using a $K_d$ of $5 \times 10^4$, and the known concentration of suspended particulates in the lake as around 0.5 ng/L, they calculated that the relative amounts of PCBs in particulates versus water would be 0.07 and 2.6 ng/L, respectively. Thus the water phase could account for more than 97% of the total PCBs in a litre of Lake Superior water. The measured total PCBs in a whole water sample from the lake is approximately 1.8 ng/L, which supported these calculations.

Frank *et al*. (1981b) collected and analyzed suspended particulates from the mouths of a large number of Canadian streams flowing into Lakes Ontario, Erie and Huron. Samples were collected by a Westfalia KDD60S continuous flow separator. All of the 105 streams sampled contained suspended solids contaminated with DDT, its metabolites, and PCBs. The highest mean concentration of total DDT was 365 ppb for streams draining to Lake Ontario from the Niagara Peninsula. The highest suspended particulate loadings of DDT were in streams with the greatest suspended sediment loads. The highest concentration of PCBs on suspended particulates was 191 ppb and came from an urban-industrial area on the shores of Lake Ontario. Of the main chemicals analyzed, DDT, PCBs and dieldrin (Table 4) were detected. From the chemical data for the 105 streams and from the total annual suspended particulate loads of the streams, the total particulate loads of various chemicals to sections of the lower Great Lakes were calculated (Table 5). Frank *et al*. (1979a) and Frank *et al*. (1981b) conducted similar river mouth surveys to determine the quantities of

**Table 4. Residues of Organochlorine Compounds in River Mouth Suspended Particulates Flowing into Lake Ontario (spring melt)**

| Location | Stream | Content in dried suspended solids (µg/kg)[1] | | | | Average annual suspended solids discharge (metric tons/year) |
|---|---|---|---|---|---|---|
| | | ΣDDT | HEoD | HCB | PCB | |
| North Shore, Lake Ontario | Butler Creek | 31 | 0.5 | | 120 | 288 |
| | Salem River | 49 | <0.1 | | 70 | 44 |
| | Colbourne Creek | 18 | <0.1 | | 500 | 465 |
| | Shelter Valley Creek | 18 | 1.0 | | 80 | 684 |
| | Cobourg Creek | 33 | <0.1 | <1.0 | 80 | 2 188 |
| | Wilmot Creek | 7 | 0.5 | | 130 | 1 177 |
| | Oshawa River | 97 | 0.5 | | 120 | 1 925 |
| | Pringle Creek | 2 | <0.1 | | NC[2] | 263 |
| | Lynde Creek | 19 | 3.0 | | 120 | 2 663 |
| | Duffin Creek | 17 | 0.5 | <1.0 | 20 | 341 |
| | Rouge River | 46 | 4.0 | | 150 | 4 768 |
| | Humber River | 12 | <0.1 | | 230 | 18 612 |
| | Mimico Creek | 15 | 4.0 | | 20 | 1 735 |
| | Etobicoke Creek | 11 | <0.1 | | 200 | 3 564 |
| | Credit River | 8 | <0.1 | | 120 | 12 625 |
| | Oakville Creek | NC[2] | <0.1 | | 1000 | 4 454 |
| | Bronte Creek | 3 | 0.5 | | 100 | 5 606 |
| Mean[3] | | 24 | 1.0 | 2.3 | 191 | |
| S.D.[4] | | 24 | 1.3 | – | 242 | |

[1] No chlordane or endrin or organophosphate insecticides were identified in suspended solids.

[2] Not calculated.

[3] Arithmetic mean.

[4] Standard deviation.

After Frank *et al.* (1981b).

**Table 5. Crude Loadings Calculated from Concentrations of Contaminants in Suspended Particulates and Mean Annual Discharges**

| Lakes and lake sections | No. of streams | Suspended solids loading (metric tons/yr) | Crude loadings (g) | | |
|---|---|---|---|---|---|
| | | | ΣDDT | Dieldrin | PCBs |
| Bay of Quinte, Lake Ontario | 7 | 50 676 | 911 | 19.2 | 1873 |
| North Shore, Lake Ontario | 23 | 89 529 | 1458 | 135 | 1293 |
| Southwest Shore, Lake Ontario | 12 | 8 352 | 1002 | 26.7 | 1520 |
| Niagara River tributaries | 5 | 1 406 | 72.9 | 0.57 | 141 |
| North Shore, Lake Erie | 18 | 154 135 | 6866 | 240 | 5914 |
| Detroit River tributaries | 3 | 12 047 | 427 | 51.6 | 1024 |

After Frank *et al.* (1981b).

Triazine residues and PCBs carried to the Great Lakes by suspended particulates in small streams and rivers in Canada. The highest mean concentration of Triazine residues (4 µg/L) occurred in stream water entering Lake Erie. Triazine has a low $K_d$, and no Triazine residues were detected in any of the suspended particulate samples. Frank *et al.* (1981b) determined concentrations of PCBs and various pesticides, including DDT, dieldrin, chlordane and Triazine in the Grand River, which has the largest drainage basin on the Canadian side of the Great Lakes (Table 6). Only known persistent chemicals were detected at the river mouth, although many known non-persistent pesticides were also detected near sites of application shortly after spraying. Polychlorinated biphenyls were found throughout the basin, and the loss of PCBs at the mouth of the Grand was around 35 kg/year. No mirex was detected at the Grand River mouth. Triazine was the most widely used pesticide, but only 0.6% of that applied appeared to reach the mouth of the Grand River. From concentration and from flow and suspended particulate load data, the aqueous and suspended particulate phase loads of the Grand and the Saugeen rivers (Table 7) were calculated (Frank, 1981).

**Table 6. Concentrations of Persistent Pesticides and PCBs in Bottom Sediments, Suspended Particulates and Whole Water at the Mouth of the Grand River, Ontario**

| Year | Chemicals | River bed sediments[1] (µg/kg [ppb]) Mean | River bed sediments[1] (µg/kg [ppb]) Range | Suspended sediments (µg/kg [ppb]) Mean | Suspended sediments (µg/kg [ppb]) Range | Whole water (ng/L [ppt]) Mean | Whole water (ng/L [ppt]) Range |
|---|---|---|---|---|---|---|---|
| 1975-76 | ΣDDT | | | 10 | 5-15 | 2.7 | ND-24 |
| | Chlordane | (AS BELOW) | | 2 | 1-3 | 0.4 | ND-5 |
| | Dieldrin | | | 0.9 | ND-1.9 | 0.7 | ND-4 |
| | Heptachlor epoxide | | | 4.7 | ND-9.4 | 0.07 | ND-1 |
| | PCBs | | | 56 | 23-80 | 5.8 | ND-100 |
| | No. of samples | | | | | 20 | |
| 1976-77 | ΣDDT | 21 | ND-60 | 13 | ND-65 | 1.5 | ND-15 |
| | α-BHC | 3 | ND-10 | 2 | ND-10 | ND | ND |
| | Chlordane | 6 | ND-17 | 4.5 | ND-3 | 0.1 | ND-1 |
| | Dieldrin | 2 | ND-5 | 0.3 | ND-3 | 0.4 | ND-2 |
| | Endrin | 1 | ND-2 | ND | ND | 0.1 | ND-1 |
| | Heptachlor epoxide | 1 | ND-3 | 0.3 | ND-3 | 0.03 | ND-1 |
| | PCBs | 25 | ND-40 | 70 | 2-120 | 3.7 | ND-100 |
| | No. of samples | 3 | | 19 | | 30 | |

[1] Values for bottom sediments determined only once.

ND – Not detected.

After Frank (1981) and Frank *et al.* (1981b).

**Table 7. Percent Loadings of Pesticides and PCBs by Particulates at the Mouths of the Grand and Saugeen Rivers, and Entering Lakes Erie and Huron, Respectively**

| Pesticides* and PCBs | At river mouths (kg/yr) 1975-76 Suspended solids | 1975-76 Water phase | 1975-76 Percent in particulates | 1976-77 Suspended solids | 1976-77 Water phase | 1976-77 Percent in particulates |
|---|---|---|---|---|---|---|
| Grand River | | | | | | |
| α-BHC | 0 | 0 | 0 | 1.0 | 0 | 100 |
| Chlordane | 0.67 | 1.09 | 38 | 2.26 | 0.21 | 91 |
| ΣDDT | 3.34 | 7.36 | 31 | 6.53 | 3.08 | 68 |
| Dieldrin | 0.30 | 1.91 | 14 | 0.15 | 0.82 | 15 |
| Endrin | 0 | 0.27 | 0 | 0 | 0.21 | 0 |
| Heptachlor epoxide | 1.57 | 0.19 | 89 | 0.15 | 0.06 | 71 |
| Lindane | 0 | 0 | 0 | 0.20 | 0 | 100 |
| PCBs | 18.7 | 15.8 | 54 | 35.1 | 7.6 | 82 |
| Simazine | 0 | 3.27 | 0 | 0 | 0.62 | 0 |
| Saugeen River | | | | | | |
| Chlordane | 0.39 | 0.22 | 64 | 0.49 | 0.38 | 56 |
| ΣDDT | 1.17 | 0.44 | 73 | 0.82 | 0.76 | 52 |
| Dieldrin | 0.04 | 0.22 | 15 | 0.11 | 0.15 | 42 |
| Heptachlor epoxide | 0 | 0 | 0 | 0.16 | 0.10 | 62 |
| PCBs | 7.0 | 0.5 | 93 | 10.3 | 0.6 | 94 |

*No endosulfan or mirex were detected in the Grand River. No endrin, lindane or simazine were detected in the Saugeen River.

After Frank (1981).

## MERCURY AND METHYLMERCURY TRANSPORT IN THE WABIGOON RIVER SYSTEM

In Canada, the site where transport, burial, recycling and bioaccumulation of a single metal has been studied in most detail is the Wabigoon-English River System of northwestern Ontario (Fig. 13). The river exits Wabigoon Lake, passes through the town of Dryden and eventually reaches Lake Winnipeg some 160 km to the west. Dryden is the site of a pulp and paper mill operation and was the site of a chloralkali plant, which operated from 1963 to 1970. By 1970, some 10 metric tons of Hg was released to the river. In 1970, input of mercury was reduced by 99%, and in 1975, the plant was converted to a non-mercury process.

In this river, as for PCBs in the Hudson River, there is a critical flow at which suspended solids are at a minimum value (Fig. 14). Above this critical value, the suspended solids concentration increases with flow because of bottom sediment resuspension. Below this value, suspended load increases primarily owing to primary productivity during the lower flow, warmer summer months. Parks *et al.* (1984) have conducted extensive studies of mercury movements in the river. The highest total Hg concentrations in suspended sediments (Fig. 15) and the highest loads of total Hg (Fig. 16) occur in the spring runoff period in April and May at sites on the mainstem Wabigoon River downstream from Dryden. In the low-flow periods there is a positive relationship between total Hg in the water and total Hg in the suspended particulates (Fig. 17). Total annual Hg *loading* in the Wabigoon River increases downstream because resuspension of bottom sediments and regeneration of Hg (and methyl-Hg) increases downstream with flow. Total Hg load increases to Clay Lake, the first major sedimentation basin

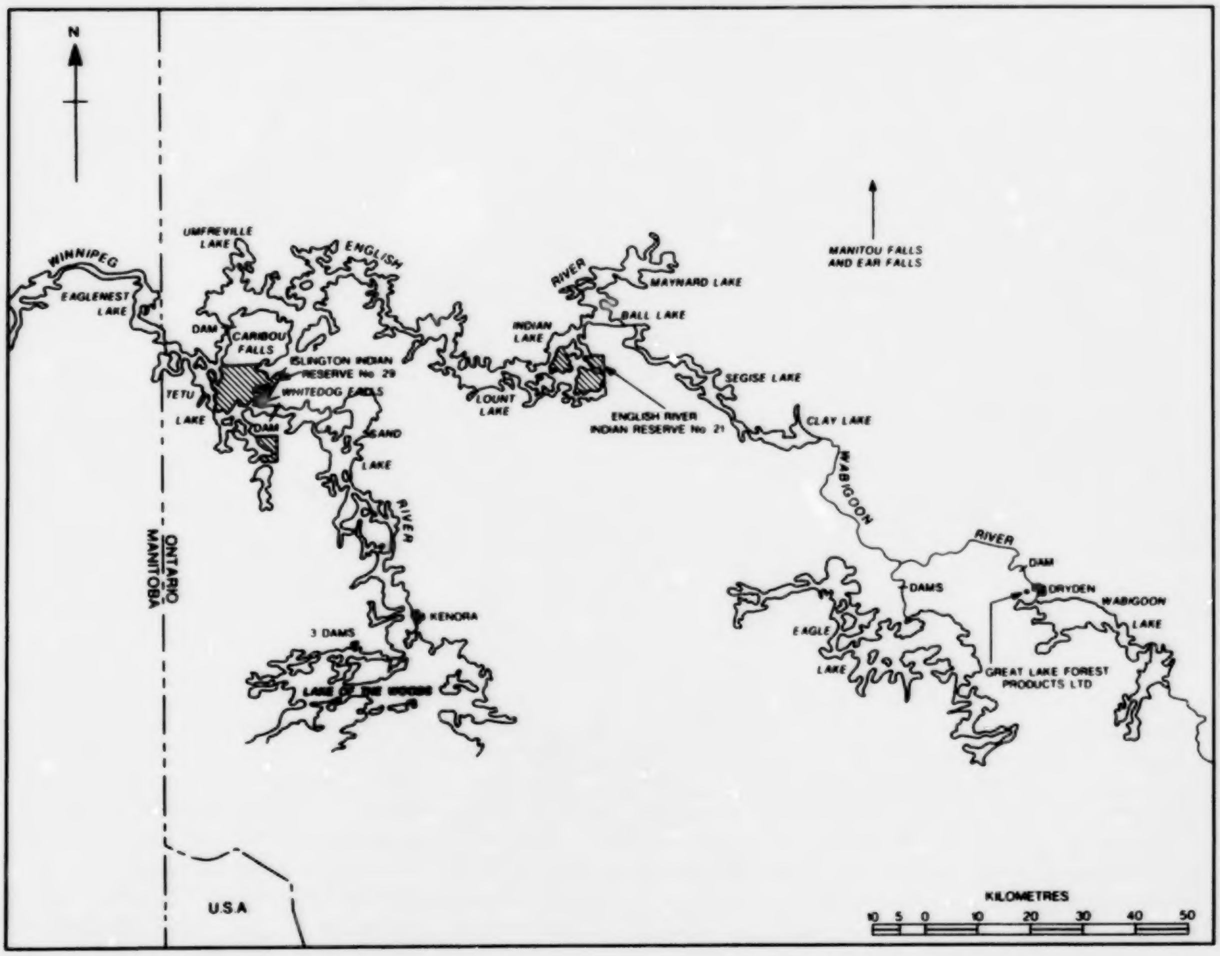
N
WINNIPEG
EAGLENEST LAKE
UMFREVILLE LAKE
ENGLISH
RIVER
DAM
CARIBOU FALLS
ISLINGTON INDIAN RESERVE No 29
WHITEDOG FALLS
TETU LAKE
DAM
SAND LAKE
RIVER
ONTARIO
MANITOBA
KENORA
3 DAMS
LAKE OF THE WOODS
U.S.A.
INDIAN LAKE
LOUNT LAKE
MAYNARD LAKE
BALL LAKE
ENGLISH RIVER INDIAN RESERVE No 21
SEGISE LAKE
CLAY LAKE
MANITOU FALLS AND EAR FALLS
WABIGOON
RIVER
DAM
DAMS
DRYDEN
WABIGOON LAKE
EAGLE LAKE
GREAT LAKE FOREST PRODUCTS LTD
KILOMETRES
10 5 0 10 20 30 40 50

**Figure 13.** The Wabigoon/English River system of northwestern Ontario (after Parks *et al.*, 1984).

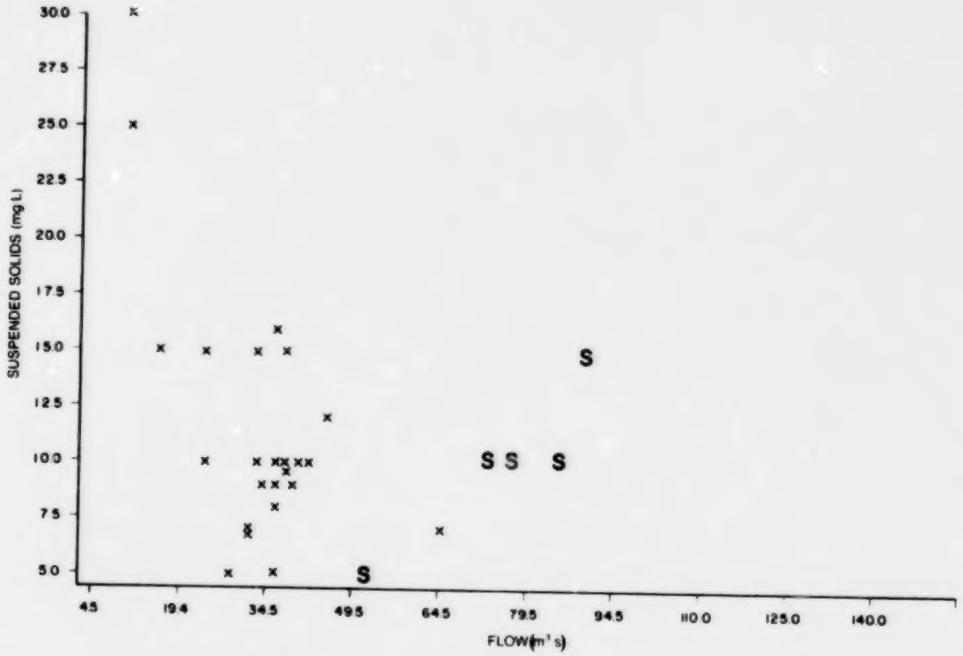

**Figure 14.** Suspended particulates vs. flow in the Wabigoon River inflow to Clay Lake (after Parks *et al.*, 1984).

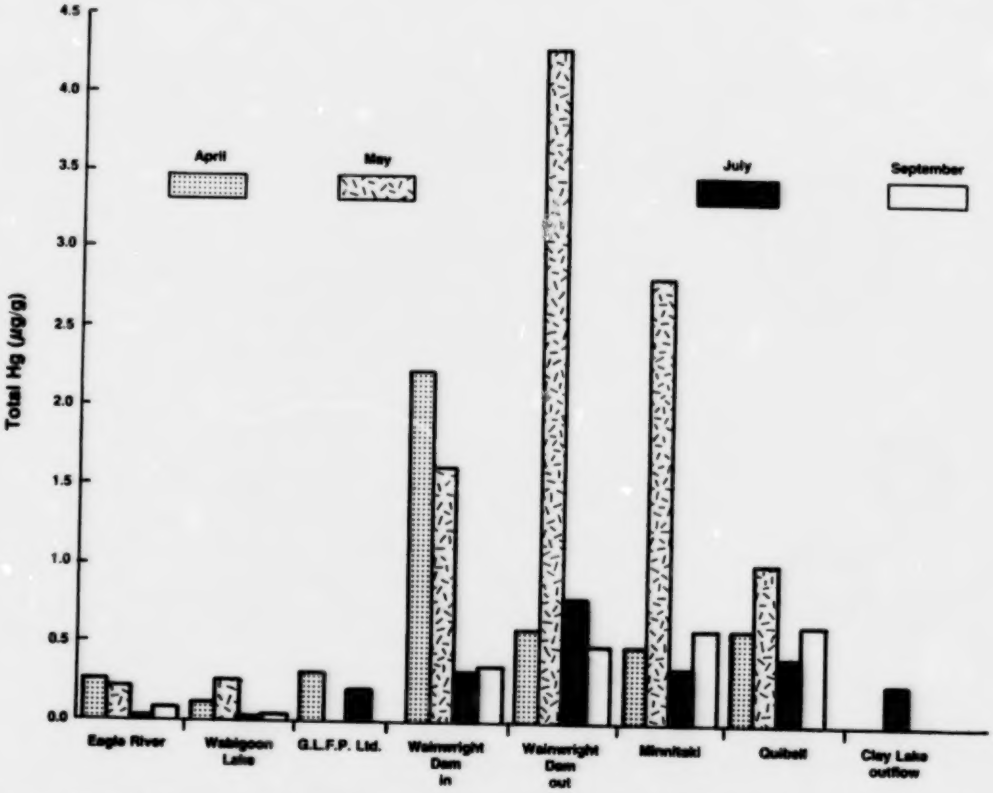

**Figure 15.** Total mercury concentrations in suspended particulates in the Wabigoon River, 1979 (after Parks *et al.*, 1984).

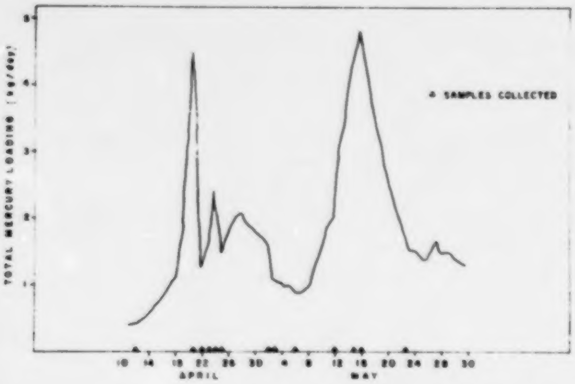

Figure 16. Total mercury loading during spring runoff at the inflow to Clay Lake (after Parks *et al.*, 1984).

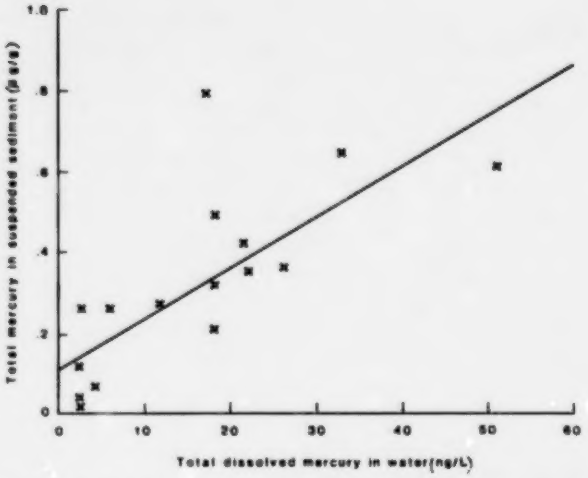

Figure 17. Relationship between dissolved and suspended particulate total mercury concentrations in the Wabigoon River system during non-high flow conditions (n = 17; r = 0.71) (after Parks *et al.*, 1984).

downstream from Dryden, where much of the particulate material is sedimented. The annual load at the inflow to Clay Lake was some 27 kg (Fig. 18). The methylmercury annual load increases mainly between Minnitaki and Clay Lake (Fig. 19) for a variety of complex reasons which control methyl-Hg production in bottom sediment. The methyl-Hg load at the Clay Lake inflow is some 1.2 kg/year or only some 4% of the annual total Hg load at that site. The methyl-Hg load, as opposed to the total Hg load, continues to increase downstream from Clay Lake.

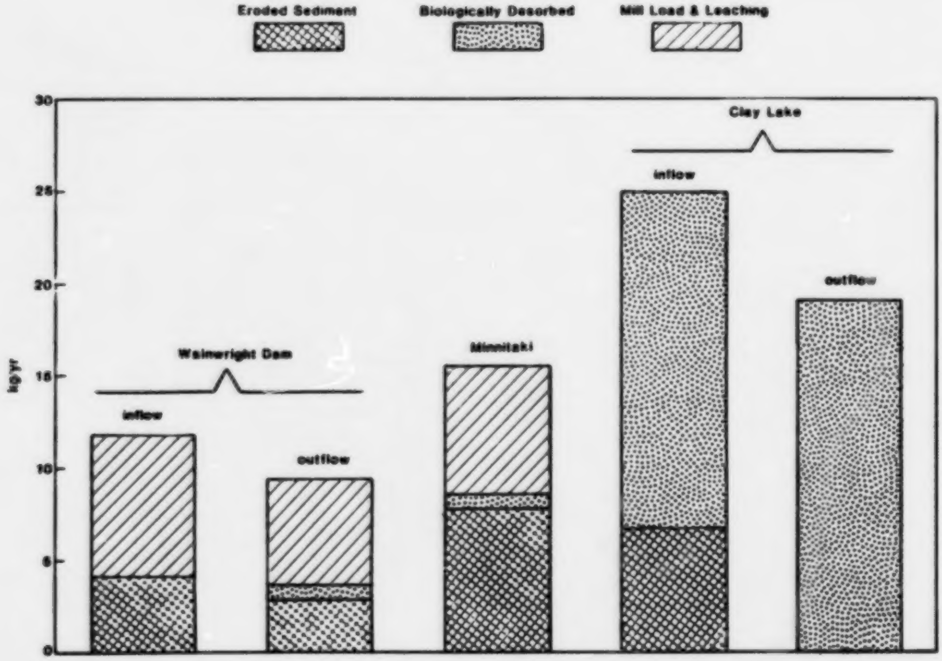

Figure 18. Mercury loadings in the Wabigoon River system, natural and anthropogenic, July 1979 to June 1980 (after Parks *et al.*, 1984).

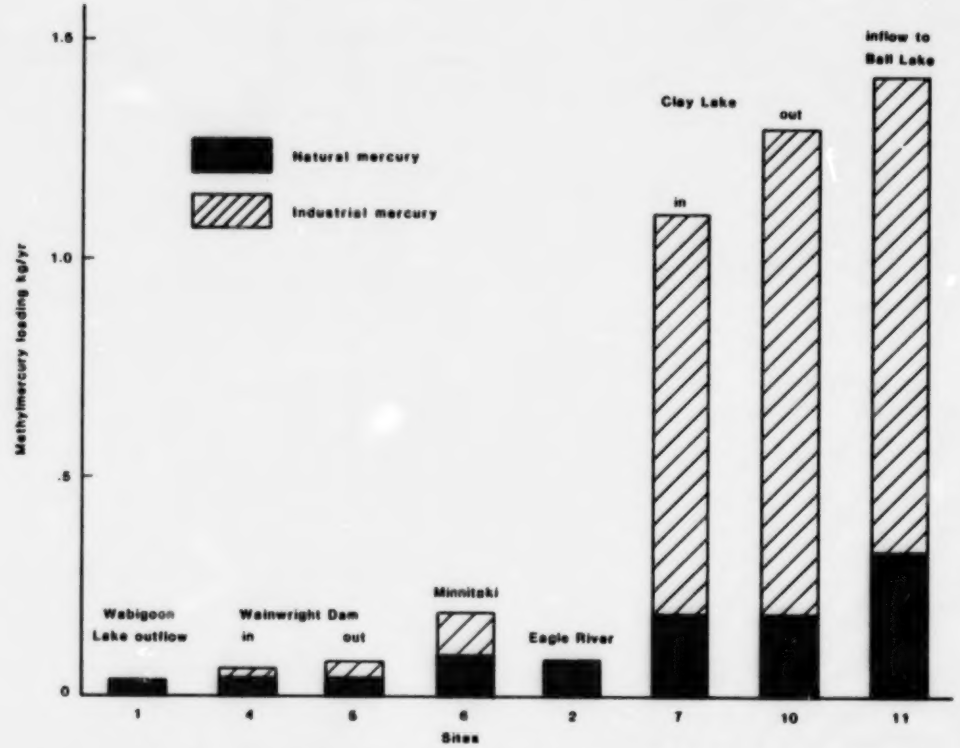

Figure 19. Natural and anthropogenically related methylmercury loadings for various sites in the Wabigoon River system, Dryden to Ball Lake, July 1979 to June 1980 (after Parks *et al.*, 1984).

Jackson *et al.* (1982) collected suspended particulates from the Wabigoon River system using high-speed centrifugation. The highest concentrations of both total and methyl-Hg in particulates occurred in the April/May high flow period (Fig. 20). Total particulate Hg and methylmercury in a given unit volume of water were also both highest in April and May (Fig. 21). The percent of the total Hg transported as methyl-Hg varied from around 1% up to 13%. The total Hg and methyl-Hg contents of the centrifuge supernatant (Fig. 22) were much less than concentrations in the particulate phase. Total Hg content of particulates varied from around 0.05 to 0.35 μg/L and methyl-Hg from nearly zero to over 18 ng/L. Total Hg content of the supernatant solution varied from around 0.01 to 0.15 μg/L and methyl-Hg from approximately zero to 15 ng/L. Using these concentrations, loadings of total and methylmercury in the particulate and "dissolved" phases were calculated (Fig. 22). The symbols on these figures refer to specific sites, and the variations between sites are important in terms of resolving the various internal sources of Hg to the system but unimportant in terms of the broad conclusions drawn here. In summer, there was a relative increase in Hg concentration in particulates in lakes. Jackson *et al.* (1982) suggested that this was due to planktonic uptake of

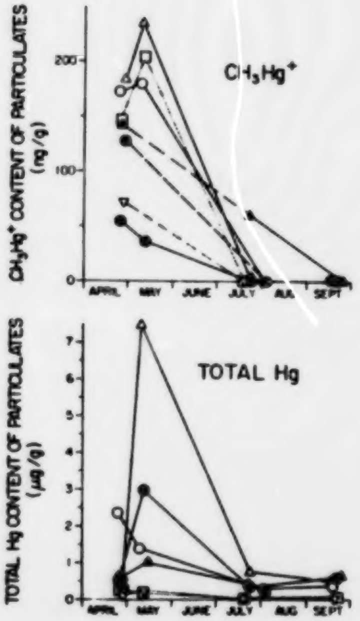

Figure 20. Seasonal variations of methylmercury and total mercury in suspended particulates (after Jackson *et al.*, 1982).

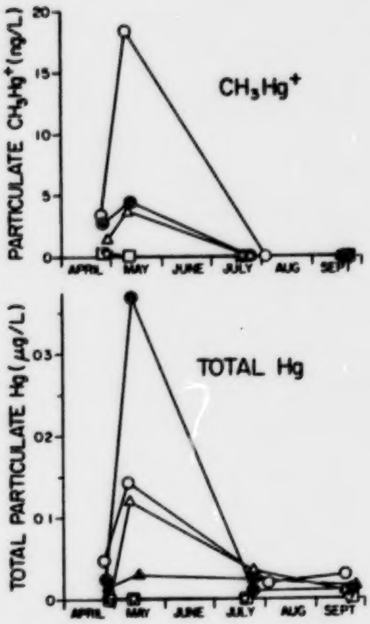

Figure 21. Particulate methylmercury and total mercury concentrations per unit volume of water (after Jackson *et al.*, 1982).

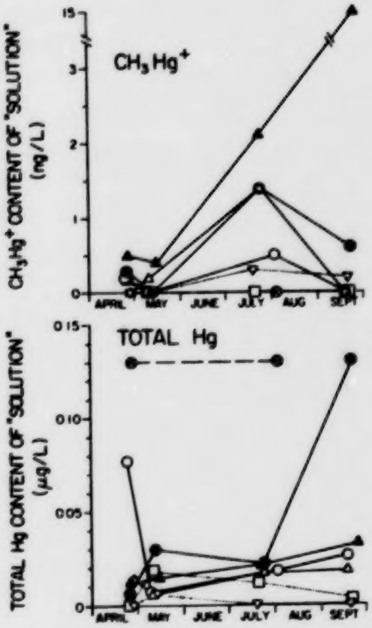

Figure 22. Methylmercury and total mercury contents of the "aqueous" phase (after Jackson *et al.*, 1982).

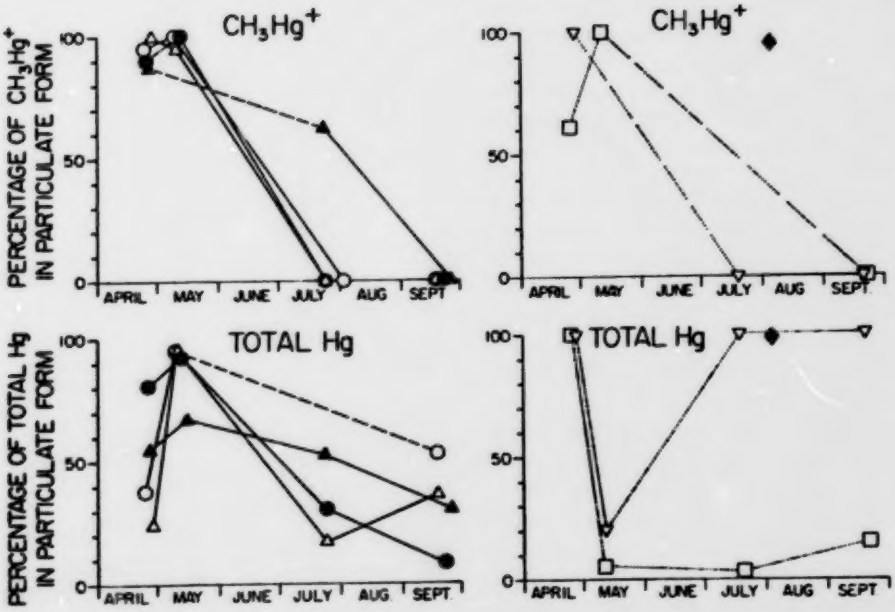

Figure 23. Percentage of methylmercury and total mercury in suspended particulates (after Jackson *et al.*, 1982).

soluble mercury. In general, increased downstream loads reflected increased discharge. Increases in methyl-Hg loads downstream are also related to discharge. However, increased methyl-Hg concentrations downstream imply that conditions for methylation or solubilization of methyl-Hg become more favourable there. Mercury and methylmercury concentrations at different sites demonstrated the complexity of the system and the continuous shifts between particulate and aqueous phases. A general assessment of the quantities of total and methyl-Hg transported in particulate form can be obtained from Figure 23. Both total particulate Hg and methyl-Hg loads in the spring can be high, over 90% in the particulate form, primarily owing to sediment resuspension. In early summer, the dissolved and particulate loads at some sites are roughly equal. In late summer (September), the soluble load can exceed the particulate load.

## TOXIC METAL AND ORGANIC CHEMICAL TRANSPORT IN THE NIAGARA RIVER/LAKE ONTARIO SYSTEM

The Niagara River flows from Lake Erie to Lake Ontario and forms part of the boundary between Canada and the United States (Fig. 24). Niagara Falls lies 35 km upstream from the in-flow site of the Niagara River to Lake Ontario. The Niagara River is one of the most polluted waterways in the world in terms of the quantity and diversity of chemicals transported to Lake Ontario. Due to the high discharge of the river, this is not reflected in absolute chemical concentrations on the basis of which water quality guidelines are set. The Niagara River is the dominant tributary of Lake Ontario, which is the source of drinking water to the greatest number of Canadians. These facts have meant that toxic organic chemical fate research in Canada has been focused in this river-lake ecosystem. New devices have been developed to sample various media in the field. State of the art capillary-gas-chromatography, capillary-gas-chromatographic/mass spectrometry, gas-chromatographic-atomic adsorption, and plasma emission techniques have been applied to the analyses of samples. Resolving the fate of contaminants in Lake Ontario can only be achieved with a sufficient understanding of the role of particulates in tracing sources of contaminants; transport of toxic metals and organic chemicals; bioavailability of contaminants; and bioaccumulation pathways.

Research into contaminant fate in polluted rivers such as the Hudson (PCBs); the James (Kepone); and the Rhine and Danube (toxic metals) is usually restricted either to one chemical and/or to the analyses of one ecosystem compartment, usually bottom sediment. The Hudson and James rivers were polluted by major chemical discharge of one chemical introduced at one point source. In both cases, the bottom sediment concentrations of the hydrophobic organic chemicals released became extreme. Bottom sediment resuspension at both sites continues to raise whole water concentrations to above detection limits at certain

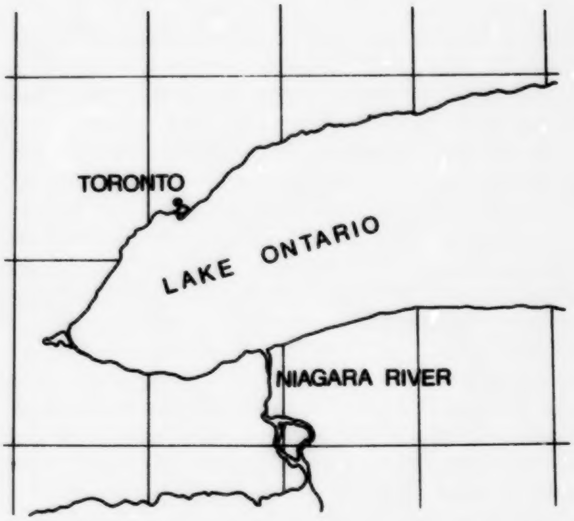
TORONTO
LAKE ONTARIO
NIAGARA RIVER

Figure 24. The western basin of Lake Ontario.

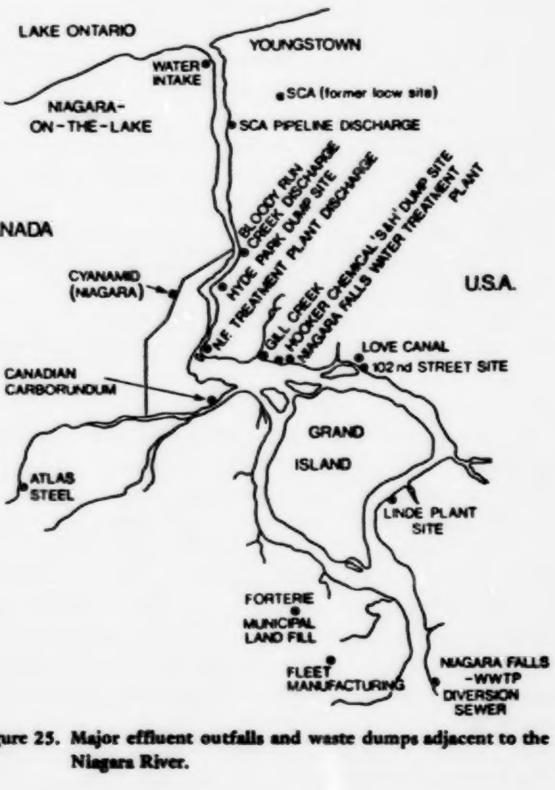
LAKE ONTARIO
YOUNGSTOWN
WATER INTAKE
NIAGARA-ON-THE-LAKE
SCA (former loow site)
SCA PIPELINE DISCHARGE
BLOODY RUN CREEK DISCHARGE
HYDE PARK DUMP SITE
N.F. TREATMENT PLANT DISCHARGE
GILL CREEK
HOOKER CHEMICAL 'S&H' DUMP SITE
NIAGARA FALLS WATER TREATMENT PLANT
CANADA
U.S.A.
CYANAMID (NIAGARA)
LOVE CANAL
102nd STREET SITE
CANADIAN CARBORUNDUM
GRAND ISLAND
ATLAS STEEL
LINDE PLANT SITE
FORTERIE MUNICIPAL LAND FILL
FLEET MANUFACTURING
NIAGARA FALLS -WWTP DIVERSION SEWER

Figure 25. Major effluent outfalls and waste dumps adjacent to the Niagara River.

times of the year, and whole water analyses can be used to determine total chemical loads. In rivers with very large discharges such as the Niagara, however, chemicals are often diluted in the whole water to levels below the detection limits for all but the best-equipped research laboratories. Because of this, new techniques for detecting pollution and contaminant transport had to be developed, and these have provided general insight into contaminant transport and fate that would not otherwise be available. The Niagara River situation is more complicated than the relatively simpler, single chemical pollution sites of the past such as the Hudson or James rivers and even Minamata Bay. It can be relatively easy, although still expensive, to study chemical transport and fate for one chemical from one source. More commonly, as in the Niagara River, multiple sources are involved (Fig. 25) and ways to try to separate these various sources and attendant inputs must be used.

Where measurable, chemical concentrations in the whole water of the Niagara River are nearly always within guidelines for drinking water standards. Thus it can be argued that the river water is usually within acceptable pollution guidelines if loads are not considered and if each chemical is considered in isolation, as in the case of the existing water quality objective setting and toxic chemical assessment procedures. The Niagara River, in fact, transports incredible loads of both toxic metals and organic chemicals. The site where the impact of these chemicals is recorded and of concern is not usually the river itself, but rather the lake into which it flows, Lake Ontario. Human consumption limits for most fish in Lake Ontario have been set for several toxic metals and persistent organic chemicals on an individual chemical basis. They include Hg, Pb, PCBs, mirex, DDT and TCDD.

Information is still required on the fate of existing chemicals in the Niagara River/Lake Ontario ecosystem. Over the past three years, in particular, much research to resolve toxic contaminant fate in Lake Ontario has been undertaken and numerous specialized publications dealing with specific aspects of this research have appeared. I will attempt here to discuss the interconnections between various types of studies undertaken in terms of contaminant-particulate interactions. I will emphasize the role of particulates as they affect the transport and burial of toxic metals and organic chemicals.

## The Pollution Problem

The Love Canal (Fig. 25) is one of the largest and most notorious chemical dumps in the United States. It is a 6.5-ha site just upstream from Niagara Falls. In 1980, the U.S. government allocated $80 million to permanently relocate 750 families living in the vicinity of the Canal. Nearby is the 102nd Street disposal site, located in Niagara Falls, U.S.A. This site required the construction of a bulkhead to prevent wastes being washed directly into the Niagara River. Closer to the Falls is the "S and H" disposal site which lies 200 m from the Niagara River and contains some ≈75 000 tons of waste liquids. Below the Falls, the 6.1-ha Hyde Park disposal site, adjacent to the Niagara Gorge, was used between 1953 and 1974 to dispose of some ≈80 000 tons of chemicals. Drainage from the Hyde Park dump followed Bloody Run Creek to the Niagara River. In recent years, remedial leachate collection systems and test wells have been constructed at all of these sites. In total, some 215 chemical waste disposal sites have been identified in New York State within 10 km of the Niagara River.

At present, there are also several major chemical outfalls along the Niagara River (Fig. 25). The two largest point sources that have received the most public attention are the outfalls of the Niagara Falls, U.S.A., Wastewater Treatment Plant immediately below Niagara Falls and the SCA Chemical Waste Services Facility pipeline near Lake Ontario. The Niagara Falls sewage treatment plant began operation with carbon absorption beds in 1977, but by 1978, the beds had been destroyed by the materials passing through them and had to be taken out of operation. Between 1978 and 1983, waste water has received only primary treatment because without these beds, the domestic and industrial wastes carried to the plant do not receive secondary treatment. Steps have recently been taken to reconstruct these beds. At the SCA site at Model City, N.Y., solid wastes are landfilled and liquid wastes undergo various physical/chemical treatments, then are transferred to facultative ponds and eventually discharged by pipeline to the Niagara River.

## Transport of Toxic Chemicals in the Niagara River/Lake Ontario System

Water quality monitoring has traditionally relied on measurement of chemicals in "solution" or in whole water. As shown earlier, depending on the quantity and type of suspended particulates, a significant toxic chemical load may be transported in the particulate phase consisting of silt, clay, amorphous metal oxyhydrates, various precipitates, and organic material and coatings with high surface areas available for sorption. Contaminants sorbed on or contained within particulate solids constitute a separate phase in a heterogeneous system and behave differently—chemically, biochemically, hydrodynamically and toxicologically—from dissolved pollutants. Virtually all water quality models used to describe the behaviour and fate of pollutants account only for the transport and distribution dynamics of a "homogeneous" dissolved phase. It has become increasingly clear in the last few years that (1) the accurate description of the environmental transport bioaccumulation and fate of particulate-associated pollutants and (2) the impact of pollutants on food webs in aquatic ecosystems and toxicological implications to man must take into account the dynamics of transport, deposition and resuspension of particles.

Suspended load concentrations and thus load transported can vary dramatically with flow, especially in small streams. In small rivers, 85% to virtually 100% of a specific chemical can be transported on the suspended particulate phase. Even in very large rivers such as the Niagara, the suspended load may vary by up to 100%, depending on resuspension related to wind events in the eastern basin of upstream Lake Erie. Such variations in sediment load can have profound effects on contaminant partitioning and fate.

Bed load transport of contaminants must also be considered, but as yet there is still no valid way to quantify this process. In the Mississippi River, the bed consists of dunes 10 m in height. Modelling the fate of a chemical spill in the Mississippi must take these dunes into account because chemicals will pool between dunes or ripple crests (Fig. 26). Many of the larger rivers of the world, such as the Fraser River in British Columbia, have such bed forms.

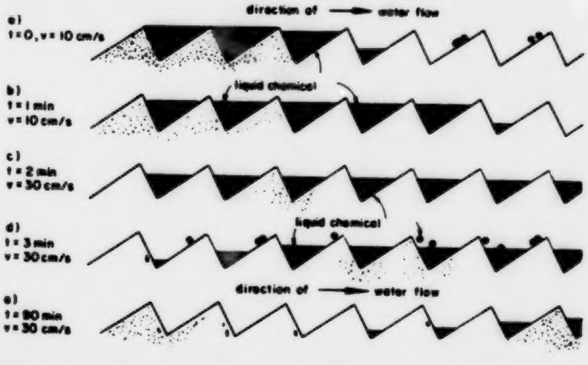

Figure 26. Effect of bottom sediment dunes on pooling of chemical spills into rivers.

Sampling of "soluble" and "suspended particulate phases" in the Niagara River and Lake Ontario has involved several state of the art techniques which have resulted in general insight into the relative importance of particulates in the transport and fate of toxic contaminants. The frequency of sampling has been intense relative to other sites and the number of chemicals investigated has been extensive. I intend to select only examples from the large volume of information available in publications and reports (COA, 1981; Allan *et al.*, 1983) or generously made available to me in manuscript form (McCrea, 1983; Kuntz, 1984) to support hypotheses to be tested by further investigation in the Niagara River/Lake Ontario ecosystem and which may assist others in investigations of similar processes in other polluted rivers and lakes.

### *Transport in the "Aqueous" Phase*

Maximum toxic metal concentrations in whole water samples taken at 1.5-m depth in the Niagara River are in the parts per billion range (µg/L): arsenic, 3 ppb; cadmium, 0.4 ppb; chromium, 260 ppb; copper, 29 ppb; lead, 5 ppb; mercury (filtered), 0.6 ppb; nickel, 40 ppb; zinc, 30 ppb. These maximum values can be compared with mean whole water (ambient) toxic metal concentrations (Table 8) obtained between 1978 and 1981. Although maximum concentrations are at levels that are easily measured, most samples contained levels beneath the detection limits. During November 1980, intensive sampling showed that there were considerable variations in the concentrations of toxic metals in whole water on a day-to-day basis. For example, chromium varied from 2 to 7 ppb over a ten-day period. The mean for ten days was 3 ppb. The results for Pb ranged from 1 to 4 ppb with a mean of 2 ppb. If these numbers were realistic, then loads varied by 3.5 to 4 times for Cr and Pb over a ten-day period.

Table 8. Trace Metal Concentrations in Ambient Water of the Niagara River at Niagara-on-the-Lake

| Element | Number of samples | Mean (ppb [µg/L]) | Range (ppb [µg/L]) |
|---|---|---|---|
| Mercury | 145 | 0.05 | 0.05–0.36 |
| Arsenic | 86 | 0.5 | 0.4–0.9 |
| Cadmium | 219 | 1 | 1–10 |
| Lead | 219 | 1 | 1–8 |
| Chromium | 216 | 2 | 1–10 |
| Copper | 219 | 4 | 1–23 |
| Zinc | 219 | 4 | 1–20 |
| Nickel | 218 | 2 | 1–13 |

Whereas toxic metals in whole water are detectable in the low parts per billion (µg/L) range, the detectable levels of whole water organic chemicals need to be at the low parts per trillion (ng/L) range. Only since the late 1970s has routine instrumentation become available for measurement of such low concentrations of chlorinated hydrocarbons. The mean and maximum whole water concentrations for the toxic organic chemicals selected for eventual comparison in several media are given in Table 9. The values found elsewhere in the literature are in the same general range. Mean concentrations are calculated by deciding what nondetection (ND) means. Usually ND is taken as zero, but some researchers prefer to use 50% of the detection limit. When NDs are taken as zero, the 1980 whole water concentrations based on 2-L samples from Niagara-on-the-Lake (site of the inflow of the Niagara River to Lake Ontario) were lindane, 4 ppt, detected in 100% (of the samples); total PCBs, 10 ppt, in 93%; HCB, 1 ppt, in 54%; total DDT and metabolites, 1 ppt, in 10%; and mirex, 1 ppt, in 0%. Monitoring of such low concentrations in whole water is not satisfactory. The high flow of the Niagara River made the use of mean whole water concentrations for load calculations somewhat dubious when detections often occurred in less than 50% of the samples. To improve monitoring and gain a better understanding of transport mechanisms, new sampling techniques were developed and have been increasingly applied in the last three years.

**Table 9. Concentrations of Total PCBs and Other Organochlorines in Raw Water at Niagara-on-the-Lake (1980–81)**

| Chemical | Mean (ppt [ng/L]) | Percent detected |
|---|---|---|
| Total PCB's | 20 | 97 |
| Lindane | 2 | 99 |
| p,p-DDT | 0.2 | 40 |
| HCB | 0.8 | 95 |
| Mirex | <0.1 | 1 |

After Kuntz and Warry (1983).

To obtain more accurate toxic organic data, especially for the lower chlorinated benzenes which can be lost in the sample work up normally used, Oliver and Nicol (1984) collected 16-L whole water samples to follow weekly organic chemical trends in the Niagara River. Two stations were sampled, one at the Niagara River inflow at Fort Erie and the other at the outflow at Niagara-on-the-Lake. Samples were collected using a magnetic drive submersible pump. The intake lines of 1.9-cm black polyethylene tubing were anchored 30 m from shore in the main river current at a depth of 13 m and about 6 m above the river bottom. The analyses of samples taken directly from the river and from the sampling device were compared and found to be in excellent agreement. The extraction procedure was optimized for the chlorobenzenes (CBs), and due to this, recoveries for other chemicals were often poorer. The sample extracts were analyzed on a Varian 4600 gas chromatograph with Vista 402 integrator and electron capture detectors using two 25-m capillary columns, a typical example of the instrumentation required for the organic chemical analyses referred to in this review. A wide concentration range and a large standard deviation were found for most compounds. The detection limits for α-BHC and PCBs were 20 and 40 to 80 ppq (pg/L), respectively. The detection limit for mirex in these 16-L samples was 60 ppq (pg/L). For some chemicals (1,2-DCB; HCB [Fig. 27]; PCT), the median value was much less than the mean value because of large concentration spikes in some of the weekly samples. Hexachlorobenzene and 1,2,3,4-TeCB and relatively constant backgrounds well above the detection limits of 10 and 20 pg/L (ppq), respectively. Numerous large peaks for DCB and TeCB (Fig. 27) probably related to pulses from point sources. Background levels for α-BHC and total PCBs (Fig. 27) were more variable and the week-to-week variations more random, perhaps because a large proportion of these chemicals enter the Niagara River from upstream (Lake Erie) and most likely come from diffuse sources. The inflow concentrations of α-BHC and PCBs to the Niagara River may also be affected by limnological processes in Lake Erie, especially wind-generated sediment resuspension. Thus, for significant measurements of most of the CBs, CTs, PCBs and mirex, the detection limits in whole water should be no higher than 0.08 ng/L and preferably no higher than 0.2 ng/L for most isomers. At these extreme detection levels of 0.01 to 0.5 ng/L and with 100% detection for the CBs, it is feasible to calculate accurate means and standard deviations (Table 10). Because the flow of the Niagara River is large and relatively constant at 6400 $m^3/s$, the total loads to Lake Ontario for many of the chemicals are considerable, in spite of the low concentrations. The role of particulates is also indicated, as several of the more toxic compounds (PCB, mirex, DDT, CBs, CTs) measured at extremely low concentrations in total water are highly partitioned onto particulates. No attempt was made to measure TCDD in whole water even though this has become the most recently discovered toxic organic chemical bioaccumulated in Lake Ontario to levels at which human consumption guidelines had to be set for top predator fish.

**Table 10. Concentrations of Chlorinated Benzenes in the Niagara River at Niagara-on-the-Lake**

| Compound | Occurrence (%) | Range | Mean ± S.D. |
|---|---|---|---|
| Chlorobenzenes | | | |
| 1,3-DCB | 100 | 2.1–110 | 11 ± 13 |
| 1,4-DCB | 100 | 9.0–310 | 36 ± 37 |
| 1,2-DCB | 100 | 3.9–240 | 23 ± 33 |
| 1,3,5-TCB | 100 | 0.19–6.8 | 0.84 ± 0.86 |
| 1,2,4-TCB | 100 | 5.8–120 | 16 ± 16 |
| 1,2,3-TCB | 100 | 1.4–30 | 3.5 ± 3.4 |
| 1,2,3,5-TeCB | 100 | 0.10–1.4 | 0.41 ± 0.23 |
| 1,2,4,5-TeCB | 100 | 0.39–9.3 | 2.0 ± 1.3 |
| 1,2,3,4-TeCB | 100 | 1.4–36 | 4.5 ± 4.2 |
| QCB | 100 | 0.34–6.4 | 1.3 ± 1.0 |
| HCB | 100 | 0.16–29 | 1.1 ± 2.9 |

After Oliver and Nicol (1984).

Because of the need to obtain routine accurate measurements of "aqueous" (non-particulate associated) organic chemicals, the Aqueous Phase Liquid-Liquid Extraction system (APLE) was developed for field use (McCrea, 1982). The APLE (Fig. 28) is primarily a stainless steel

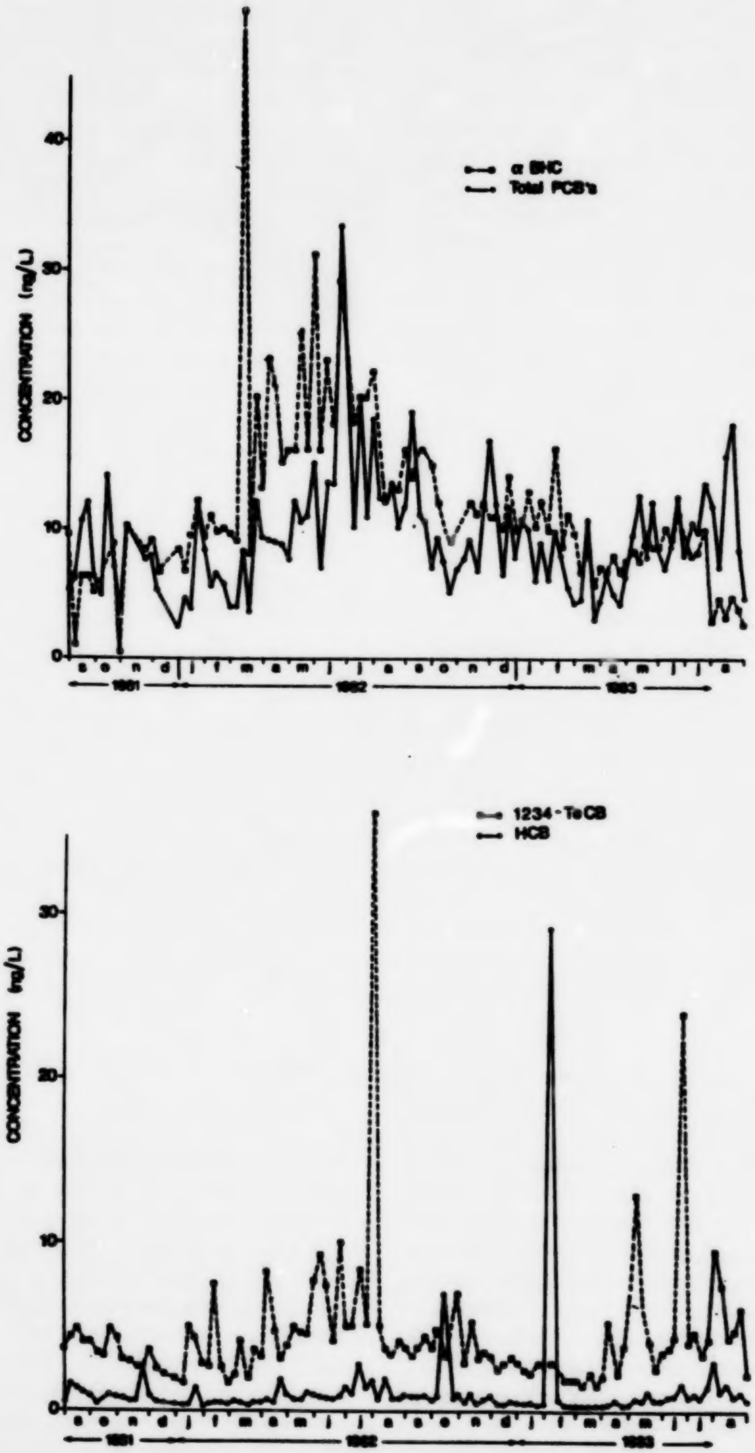

**Figure 27.** Distribution of α-BHC, total PCBs, 1,2,3,4-TeCB and HCB in whole water at Niagara-on-the-Lake (after Oliver and Nicol, 1984).

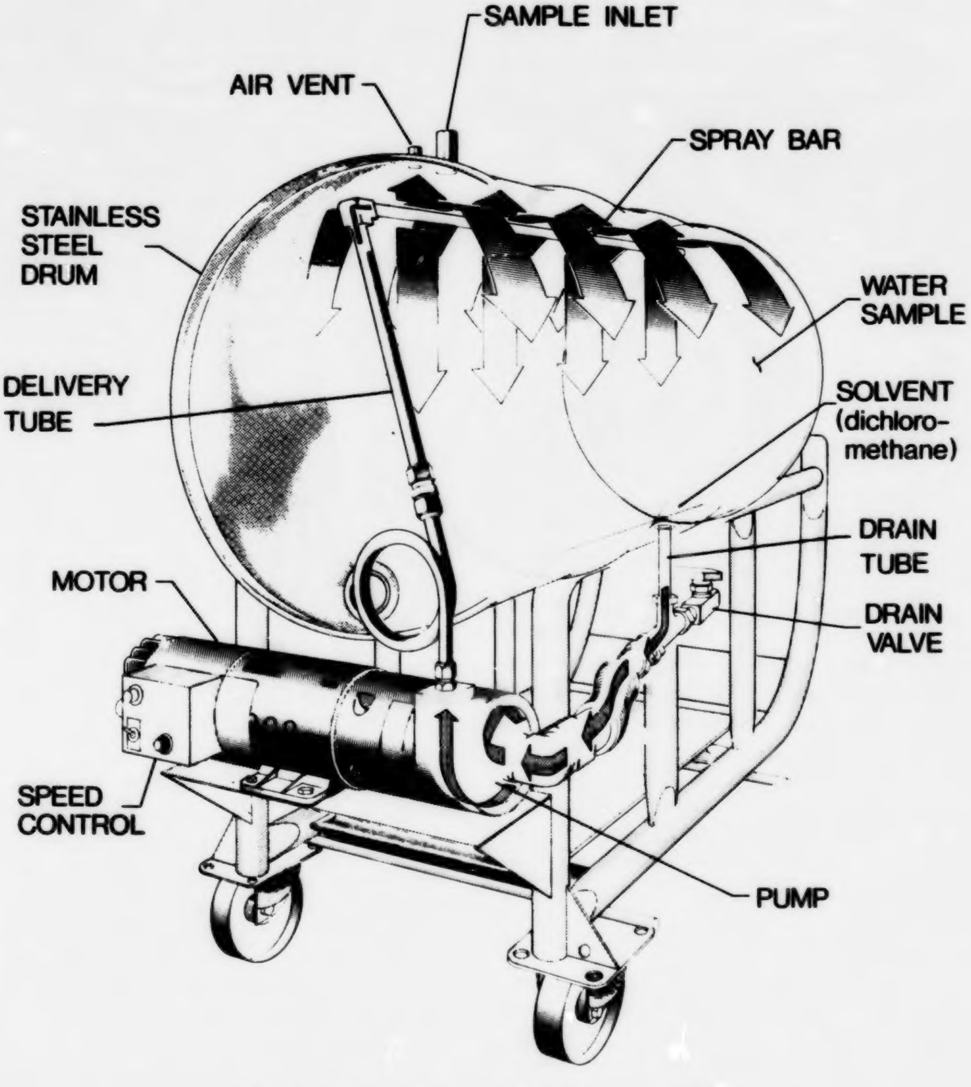

Figure 28. The aqueous phase liquid-liquid extractor (APLE).

45-gallon drum, in which the extractant (solvent) is sprayed from a bar at the top of the drum, collects at the bottom, and is continuously pumped back to the spray bar. The large-volume (200 L) aqueous phase extracted is the supernatant from the high-speed Westfalia centrifuge system used to remove particulates from approximately 8000 L of water. Extraction is with 8 L of dichloromethane for 90 min with a subsequent 2-h separation period. Large seasonal and spatial variations in aqueous phase organic chemical concentrations were suspected in the Niagara River. Some APLE samples from five stations between Lake Erie and Lake Ontario have been analyzed for a large number of chemicals (Kuntz, 1984), but I will only refer here to a few selected examples. There was no specific seasonal pattern for total PCBs (Fig. 29), DCBs and TeCBs. There was, however, a distinct spatial distribution. Polychlorinated biphenyls were apparently transported into the Niagara River mainly from Lake Erie, in the aqueous phase. There were further inputs along the river, and the aqueous phase concentrations did increase, especially in November and May. Dichlorobenzenes are also loaded to the river from Lake Erie and likewise the aqueous concentrations do increase downstream but not at the same time as for total PCBs. The chemical TeCB is virtually absent in the Lake Erie inflow and until downstream from Niagara Falls. Mirex, which is highly partitioned to particulates, was detected in 6 of 11 samples at levels between 0.5 and 1.5 pg/L (ppq), which is the lowest value recorded for this chemical in water. The APLE extractor has also been used to investigate daily variations in whole water organic chemical concentrations in the Niagara River (Kuntz, 1983). Distinct peaks for most chemicals were again detected, even on this daily sampling timetable. The peaks for PCBs and HCB were seven and five times the lowest concentrations measured over the 11-day period. In summary, although aqueous phase concentrations are extremely low, the aqueous phase is still a major transport medium even for highly particulate-associated organic chemicals because of the high flow of the Niagara River. Although there is no clear seasonal pattern for organic chemical concentrations in the Niagara River, the spatial distributions of chemicals, even extremely low concentrations, can still be related to suspended source locations and types.

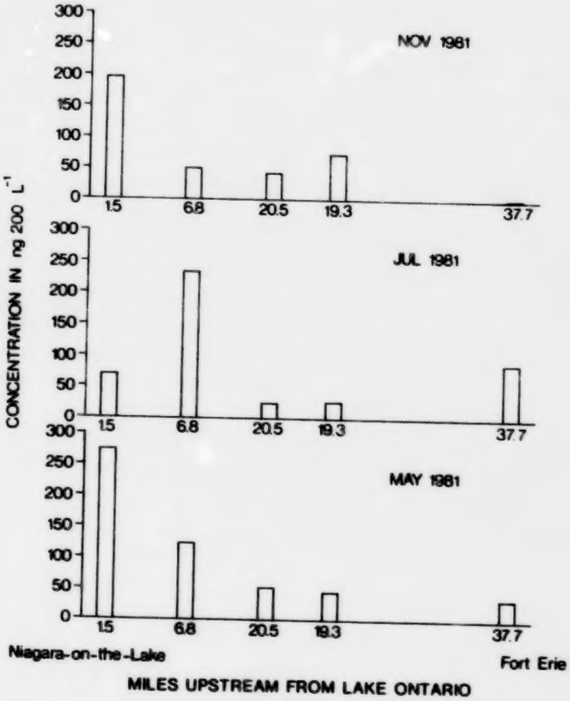

**Figure 29.** Distribution of total PCBs (ng/200 L) in the aqueous phase of the Niagara River at Niagara-on-the-Lake, 1981 (after Kuntz, 1984).

### *Particulate Phase Transport*

Most of the suspended particulates collected from the Niagara River have been separated by the Westfalia high-speed centrifuge system. The Westfalia gives some 90% to 95% efficiency in recovery of suspended loads with up to 70% particulates finer than 0.1 μm. Concentrations of toxic metals as well as toxic organic chemicals are well above detection levels in most samples. Toxic metals are usually in the parts per million (μg/g) range and organic chemicals in the parts per billion (ng/g) range. Thus, for chemicals known to be bioaccumulated in downstream Lake Ontario, suspended particulates are the preferred monitoring medium for the Niagara River.

Typical suspended particulate and bottom sediment concentrations for toxic metals in the Niagara River upstream, Lake Erie and Lake Ontario (Kauss, 1983) are given in Table 11. Earlier, Thomas (1983) had obtained comparable concentrations for suspended particulates at Niagara-on-the-Lake. Some of the contaminants entering the river from storm sewers are on particulates prior to being added to the river. Variations in concentration of chemicals in suspended particulates in the Niagara River can be used to distinguish such sources of contaminants. The suspended particulate concentrations were often high, increased on passage down the river and often exceeded dredge spoil guidelines. A comparison between suspended sediment and surficial bottom sediment concentrations at the same sites and upstream and downstream shows that for metals at some locations, there appears to be fairly good correlation, for example, for Cr, >Pb and >Zn in eastern Lake Erie. In the Niagara River, however, bottom sediments have lower concentrations than the suspended particulates because the high flow precludes extensive sedimentation of finer particles. At Niagara-on-the-Lake, the suspended particulates entering Lake Ontario have higher concentrations than the surficial bottom sediment samples from the lake. The higher organic content of the suspended load (up to 10% organic carbon) and depositional patterns within the lake may explain this difference.

Between 1978 and 1980, centrifuged suspended particulates from Niagara-on-the-Lake were routinely analyzed, in the later years on a weekly basis, for total toxic metal concentrations, including Cd, Pb and Cr (Fig. 30) (COA, 1981). As shown later, the order of percent bioavailable (easily extractable) for these metals in suspended particulates is Cd > Pb > Cr. Total toxic metal concentrations in suspended particulates over an 11-day period in 1980 indicated that there were changes in total As of around 30% (Fig. 31). These changes did not correlate with any obvious parameter such as total suspended particulate load.

Interpretation of heavy metal bioavailability in suspended particulates must consider the nature of the suspended material. Because high-speed centrifuges can destroy algae and zooplankton, the suspended "sediment" that is

**Table 11. Toxic Metals in Suspended Particulates and Surficial Sediments in Lake Erie, the Niagara River and Lake Ontario**

| Sample type | Element | Lake Erie* Basin (µg/g [ppm]) | Typical upper† Niagara River (µg/g [ppm]) | Typical lower‡ Niagara River (µg/g [ppm]) | Lake Ontario Basin (µg/g [ppm]) |
|---|---|---|---|---|---|
| Suspended sediment | As | – | 9.8 | 16 | – |
| | Cd | 6.6 | 8.2 | 3 | – |
| | Cr | 53 | 160 | 80 | – |
| | Cu | 170 | 290 | 100 | – |
| | Pb | 79 | 170 | 100 | – |
| | Hg | 0.14 | 0.73 | 0.69 | – |
| | Ni | 91 | 75 | 53 | – |
| | Zn | 160 | 870 | 330 | – |
| Surficial sediments | As | 3.2 | 1.9 | 2.5 | 3.3 |
| | Cd | 2.5 | 0.50 | 0.72 | 2.5 |
| | Cr | 53 | 11 | 15 | 48 |
| | Cu | 39 | 8.5 | 8.8 | 50 |
| | Pb | 81 | 11 | 13 | 106 |
| | Hg | 0.48 | 0.09 | 0.19 | 0.65 |
| | Ni | 49 | 6 | 7.2 | 52 |
| | Zn | 177 | 100 | 63 | 192 |

* Thunder Bay, eastern Lake Erie.
† About 8 km upstream from Niagara Falls.
‡ Niagara-on-the-Lake.

After Kauss (1983).

eventually analyzed after a large volume of water passes through the centrifuge may be highly organic and composed to a considerable degree of pulverized biotic material. Thus, interpretation of seasonal transport characteristics of particulate toxic metal loads requires that information also be available (but seldom is) on seasonal phytoplankton, zooplankton, bacterial and aquatic plant population cycles and on the decay rates of organic matter. Aquatic plants accumulate metals and on senescence, the metal-enriched organic debris is carried downstream (Blachford and Ongley, 1984). In general, the role of aquatic plants as *in situ* monitors of toxic chemical bioavailability and as eventual transport media requires greater investigation.

The suspended particulate heavy metal values obtained by Kauss (1983) and Thomas (1983) are total metal concentrations. Total metal concentrations can provide important total load information and help to detect major sources, but they are of limited value in terms of biological significance. Sequential extraction techniques to determine bioavailable content of toxic metals have been applied primarily to bottom sediments. Extractable (0.5 *N* HCl) heavy metal concentrations in suspended particulates from the

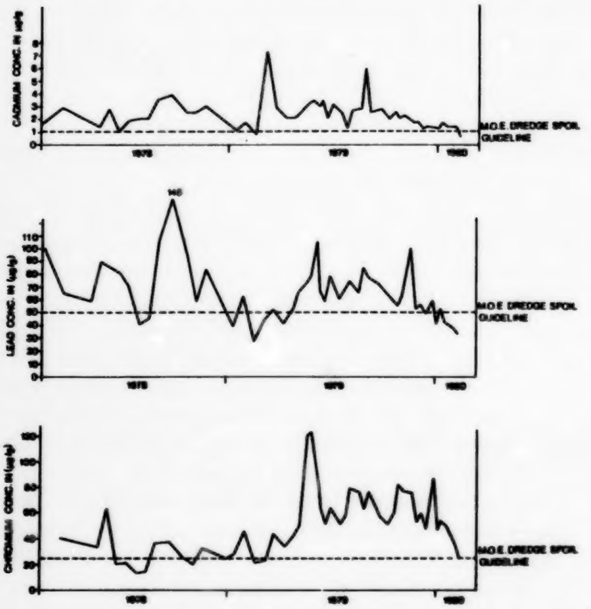

**Figure 30.** Distribution of cadmium, lead and chromium in suspended particulates in the Niagara River (after COA, 1981).

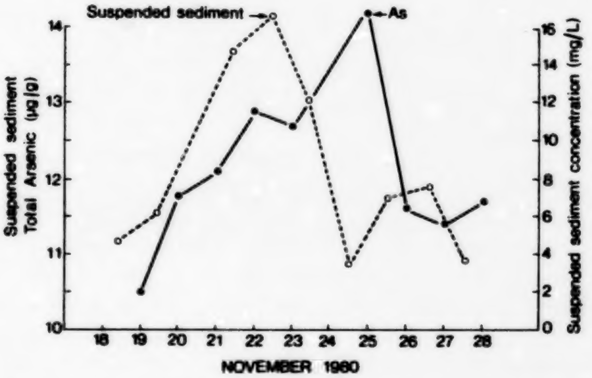

**Figure 31.** Daily suspended particulate arsenic concentration variations in the Niagara River at Niagara-on-the-Lake (after Kuntz, 1983).

Niagara River are a crude estimate of particulate toxic metal bioavailability (Kuntz, 1983) (Table 12). During an 11-day period in 1980, daily suspended particulates contained lower 0.5 *N* HCl extractable metals concentrations than the values in Table 12, but in terms of total concentrations the levels remained generally the same. Few individuals have applied complete SET to suspended particulates. One drawback is the need to use centrifuges of the Westfalia type in the field. Another is the labour-intensive analytical procedures. Lum (personal communication, 1983) has applied SET to Niagara River suspended particulates collected during 1982. When the anthropogenic labile fraction (combination of easily extractable, carbonate and surface oxide forms) is separated from the organic and residual forms (Table 13), lower percentages of total Ni, Cu, Pb and Zn were removed than by the 0.5 *N* HCl extraction. Two general conclusions can be drawn from these data:

(1) Only a small fraction, normally about 30% of the total metals present in suspended particulates, is easily extractable and

(2) Changes in suspended particulate toxic metal concentrations can occur over short periods.

In summary, large loads of toxic metals can be transported as suspended particulates even in rivers such as the Niagara, which has a low mean suspended load of only 8.4 mg/L. For many of the metals a much smaller fraction of the total is bioavailable, as measured by state of the art SET. The metals are usually predominantly present in resistant mineral and organic forms.

**Table 12. Total vs 0.5 *N* HCl Extractable Toxic Metals in Suspended Sediments at Niagara-on-the-Lake**

| Element | Total* (μg/g [ppm]) | Total† (μg/g [ppm]) | Extractable‡ (μg/g [ppm]) |
|---|---|---|---|
| As | 16 | 14 | 11 |
| Cd | 3 | 5.6 | 2.4 |
| Cr | 80 | 173 | 31 |
| Cu | 100 | 69 | 39 |
| Pb | 100 | 117 | 62 |
| Hg | 0.69 | 0.87 | 0.23 |
| Ni | 53 | 69 | 24 |
| Zn | 330 | – | 159 |

* Kauss (1983) based on one sample.
† Thomas (1983) mean of 10.
‡ Kuntz (1983) mean of 17 to 57.

Suspended particulates from the Niagara River showed the same general patterns for toxic organic contaminants (Kauss, 1983) as for toxic metals (Table 14). Concentration shifts could be used to estimate source locations. The best examples are the differences in HCB and mirex concentrations between Lake Erie and the upper river, above the suspected sources, and the lower river below these sources. A similar pattern is found in surficial bottom sediments. In downstream Lake Ontario, however, the mean surficial bottom sediment concentrations are less than those of suspended particulates in the Niagara River. Much of the suspended material is rapidly sedimented near the Niagara River inflow to Lake Ontario and over only a small fraction of the total lake bottom area. Toxic organic chemicals introduced to the river are rapidly partitioned onto suspended particulates in the river.

**Table 13. Readily Available Metals in Suspended Particulates from the Niagara River**

| Sampling date | Cd (μg/g [ppm]) | Zn (μg/g [ppm]) | Pb (μg/g [ppm]) | Cu (μg/g [ppm]) | Ni (μg/g [ppm]) |
|---|---|---|---|---|---|
| 82-06-01 | 2.4<br>(57)* | 120<br>(33) | (16)<br>(25) | 3.6<br>( 7) | 5.0<br>( 5) |
| 82-06-16 | 2.2<br>(59) | 78<br>(31) | 24<br>(17) | 3.0<br>( 7) | 6.1<br>( 5) |
| 82-06-22 | 1.1<br>(50) | 46<br>(22) | 9<br>(18) | 4.0<br>( 8) | 6.0<br>(10) |
| 82-06-30 | 1.8<br>(53) | 63<br>(27) | 18.5<br>(22) | 5.5<br>( 6) | 6.0<br>( 9) |
| 82-07-14 | 2.0<br>(74) | 40<br>(21) | 8.5<br>(14) | 2.0<br>(38) | 5.5<br>( 6) |
| 82-07-27 | 3.6<br>(86) | 75<br>(27) | 15.5<br>(15) | 11<br>(14) | 11<br>(18) |
| 82-08-09 | 1.6<br>(71) | 53<br>(23) | .16<br>(20) | 4.8<br>( 8) | 9.9<br>(18) |

*Amounts in parentheses are concentrations as percentage of total.

Source: K. Lum, personal communication, 1983.

**Table 14. Concentrations of Organic Chemicals in Suspended Particulates and Surficial Sediments in Lake Erie, the Niagara River and Lake Ontario**

| Sample type | Chemical | Location | | | |
|---|---|---|---|---|---|
| | | Lake Erie* basins | Typical upper† Niagara River | Typical lower‡ Niagara River | Lake Ontario basins |
| Suspended sediments | Total PCBs | 450 | 660 | 230 | – |
| | Lindane | ND | ND | 8 | – |
| | Total DDT + metabolites | 30 | 43 | 9 | – |
| | HCB | ND | 30 | 97 | – |
| | Mirex | 20 | 15 | 130 | – |
| Surficial sediments | Total PCBs | 86 | 960 | 2700 | 85 |
| | Lindane | – | ND | ND | – |
| | Total DDT + metabolites | 30 | 2 | 179 | 62 |
| | HCB | – | ND | 250 | – |
| | Mirex | ND | ND | 640 | 10.2 |

* Station for suspended sediments is in Thunder Bay and represents eastern Lake Erie.
† Station in Tonawanda Channel some 8 km above Niagara Falls.
‡ Station below Niagara Falls some 8 km above Lake Ontario.

ND – Not detected.

After Kauss (1983).

The routine collection of suspended sediments at Niagara-on-the-Lake was introduced as the prime technique to monitor toxic organic chemical loading to Lake Ontario in 1979 (Warry and Chan, 1981a) and produced long-term mean values and ranges for a large number of the organic chemicals (Kuntz, 1983) (Table 15). Similar values for the same chemicals were reported by Kuntz and Warry (1983) and by Thomas (1983). Polychlorinated biphenyls, mirex and HCB are three of the main hydrophobic (particulate-related) and toxic organic chemicals in Lake Ontario. Concentration changes for these organic chemicals in suspended particulates at Niagara-on-the-Lake were monitored in 1979 (Warry and Chan, 1981a) (Fig. 32). Variations are probably related to sources, namely single-point (mirex); versus multiple-point (HCB); versus diffuse (PCBs). The concentrations of toxic organic chemicals attained in suspended particulates were high and often exceeded dredge spoil guidelines (Ontario Ministry of the Environment) where these exist. Using a mean flow value of 6400 m$^3$/s and a mean suspended particulate concentration of 8.4 mg/L for the Niagara River permits load calculations that demonstrate that the suspended particulate fraction is a major

**Table 15. Organochlorine Concentrations in Suspended Sediment of the Niagara River at Niagara-on-the-Lake**

| Chemical | Detected (ppb) | Mean (ppb) | Range (ppb) |
|---|---|---|---|
| Total PCBs | 100 | 590 | 30–2700 |
| HCB | 100 | 72 | 3–442 |
| TeCB | 98 | 72 | 1–248 |
| DCB | 77 | 228 | 1–1286 |
| Mirex | 68 | 10 | 1–258 |
| Lindane | 31 | 2 | 1–27 |

After Warry and Chan (1981a).

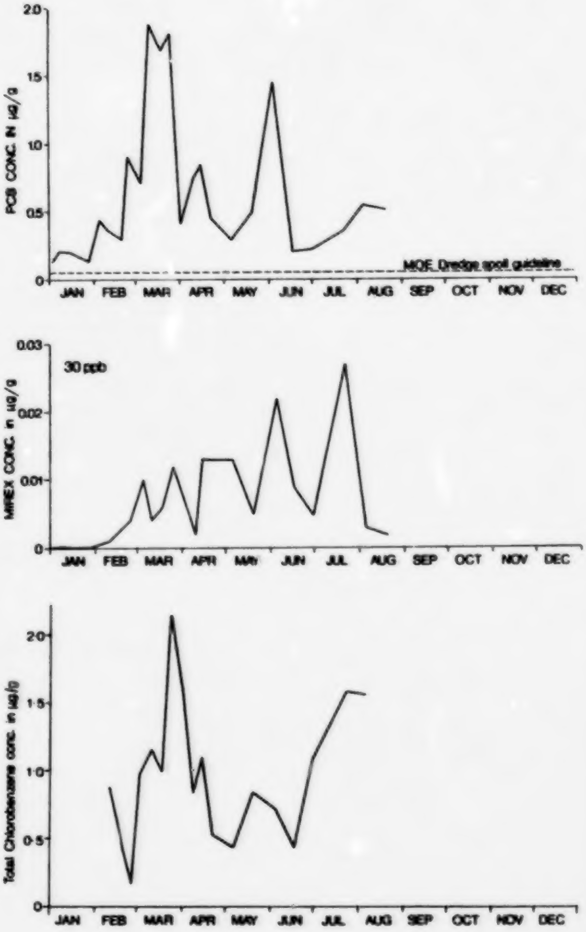

Figure 32. Distribution of total PCBs, mirex and total chlorobenzenes in suspended particulates in the Niagara River at Niagara-on-the-Lake (after Warry and Chan, 1981a).

transport medium for hydrophobic organic chemicals. Suspended particulates from the Niagara-on-the-Lake site were further collected on a daily basis for an 11-day period (Kuntz, 1983). Polychlorinated biphenyls and HCB showed only limited variation in concentrations (Fig. 33). The concentrations of PCBs were higher and of HCB about the same as found in the routine long-term program.

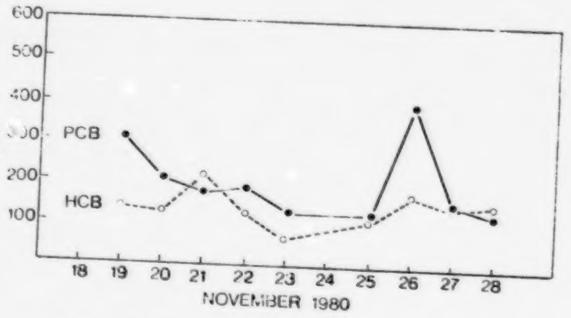

**Figure 33. Daily suspended particulate total PCB and HCB concentration variations in the Niagara River at Niagara-on-the-Lake (after Kuntz, 1983).**

Additional sampling has been carried out to determine changes in concentration of organic chemicals in suspended particulates with transport down the Niagara River. The selected results for total DDT and tetrachlorobenzenes are examples of the two most common distributions (Fig. 34) found for a large number of other organic chemicals. The first distribution type for total DDT begins with high concentrations in suspended particulates at the inflow to the river and only slight increases in concentrations downstream. Such a pattern implies loading from diffuse upstream sources. A similar pattern occurs, for example, for DCB. The second type of distribution is that for TeCB. Concentrations at the inflow and well downstream are low. However, major increases, up to greater than 80 ppb TeCB, occur in the lower river downstream from Niagara Falls and the large waste dumps mentioned earlier. The same pattern is found for mirex and for HCB and means that hydrophobic compounds are introduced in passage down the river either already bound to particulates or are rapidly partitioned onto them, perhaps in response to the turbulence below Niagara Falls and in the Niagara River Gorge (Fox *et al.*, 1983).

### *Partitioning of Toxic Organic Chemicals*

The laboratory and theoretical research described earlier reviewed various factors that influence the partitioning of organic chemicals between water, particulates and biota. The most important factor was particulate organic carbon content. This factor is akin to lipophilicity in that "sediment" partitioning has been shown to be pre-

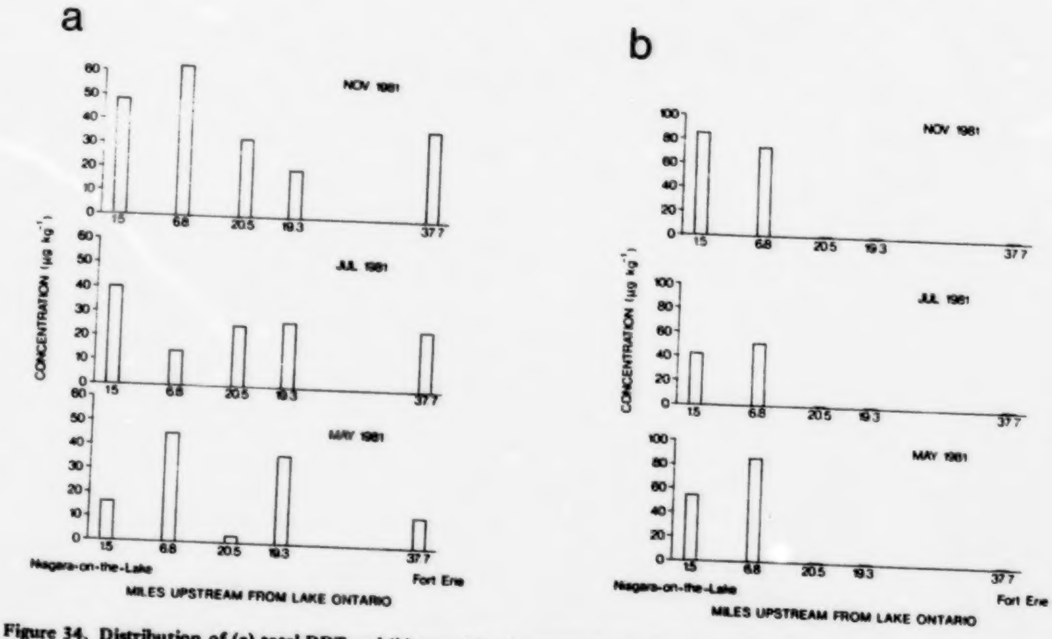

**Figure 34. Distribution of (a) total DDT and (b) tetrachlorobenzenes (µg/kg) in suspended particulates at different sites in the Niagara River, 1981 (after Kuntz, 1984).**

dictable from octanol-water partition coefficients if the organic content of the sediment is known. Data collected by the combined use of the 200-L APLE and the Westfalia high-speed centrifuge systems to resolve transport processes of organic chemicals in the Niagara River can be examined in terms of partitioning in real field situations (McCrea *et al*., 1983). The aqueous phase in the surface water of Lake Ontario contained 99.9% of chlorinated pesticides, 100% of HCB, and 91% of total PCBs. The bulk of the total organic chemicals present, many of which have low $K_d$'s, was in the aqueous phase. In the Niagara River, the concentration of organic chemicals in the particulate phase, and thus the partitioning of several hydrophobic organochlorine pesticides as well as HCB and PCBs, varied greatly over the course of the river. For example, the percentages found in the aqueous phase at different sites in the lower Great Lakes were high for total pesticides (Table 16) but lower for several of the highly hydrophobic industrial organic chemicals. The latter are presently of most concern in the Lake Ontario/Niagara River system. The lakes are also sites of partitioning of organic chemicals to particulates, followed by sedimentation and burial. The Niagara River is an active sediment transport system and a site of sediment generation above Niagara-on-the-Lake. The results show that in open lakes, most of the organochlorines are in the aqueous phase but that in the connecting channels, the amount in the particulate phase dominates for the more hydrophobic compounds (PCBs, HCB and mirex). Thus, although the resolution of fate and bioaccumulation pathways of chemicals may be controlled by particulates, the degree of this control is a function of the parameters discussed earlier and includes both the properties of the chemical and of the limnological ecosystem.

Over the course of the Niagara River, the concentration of DDT (Fig. 35) in nanograms per litre went up in the particulate phase with distance downstream. Hexachlorobenzene has a similar distribution to DDT but with the expected source above the NR 6.8 location. The aqueous phase concentrations of both DDT and HCB were higher in Lake Ontario than at the Lake Erie inflow. An example of a different extreme in organic chemical transport phase is lindane. All of the $\alpha$- and $\gamma$-BHC (lindane) was transported in the aqueous phase, and inputs along the course of the river only added to this phase (Fig. 35). Hexachlorobenzene is highly partitioned to particulates; nevertheless, the Lake Ontario aqueous phase concentration of HCB is considerably above that of both the upper Niagara River and of Lake Erie, perhaps related to desorption from settling particulates and/or sedimentation of particulates and re-establishment of a new equilibrium. Mirex deserves special mention because it was and still is one of the more serious contaminants of Lake Ontario. Mirex is extremely partitioned to particulates, yet it is found in herring gull eggs at the highest level in the aquatic food web. Mirex was not detected in any of the APLE aqueous phase extracts (McCrea *et al*., 1983). Oliver (personal communication, 1983), using the APLE, reported a mirex concentration of some 5 pg/L (ppq) in "whole water" in Lake Ontario, a value below the detection limit of McCrea *et al*. (1983).

McCrea *et al*. (1983) pointed out that most laboratory determinations of physical properties of organic chemicals are made in distilled water and that this may preclude extrapolation to complex, real aquatic ecosystems. Also, in the field, organic chemicals are usually present at three to six orders of magnitude below their saturation point, which could lessen the control of solubility on partitioning. Although field and laboratory values were not identical, the favouring on a gross scale of either the suspended particulate or the aqueous phase was in accord with the predictions that could be made on the basis of contaminant physical chemical properties. A variety of ecosystem factors could account for the differences from predicted values, including the following:

(a) Increases in suspended particulate concentrations due to biological processes

(b) Point source inputs of particulate-associated contaminants

(c) Erosion of contaminated sediments from shorelines

(d) Resuspension of contaminated bottom sediment.

**Table 16. Percent of Organochlorine Contaminants Present in the Aqueous (APLE) Phase**

| Chemical | Sites | | |
|---|---|---|---|
| | Lake Erie inflow to Niagara River (%) | Niagara-on-the-Lake (%) | Lake Ontario (3 stations) (%) |
| PCBs | 100 | 22 | 91 |
| HCB | 48 | 28 | 100 |
| Mirex | ND | ND | ND |
| p,p′-DDT | 94 | 70 | 100 |
| $\gamma$-BHC | 100 | 98 | 100 |
| Total pesticides | 85 | 78 | 99 |

ND – Not detected.

After McCrea *et al*. (1983).

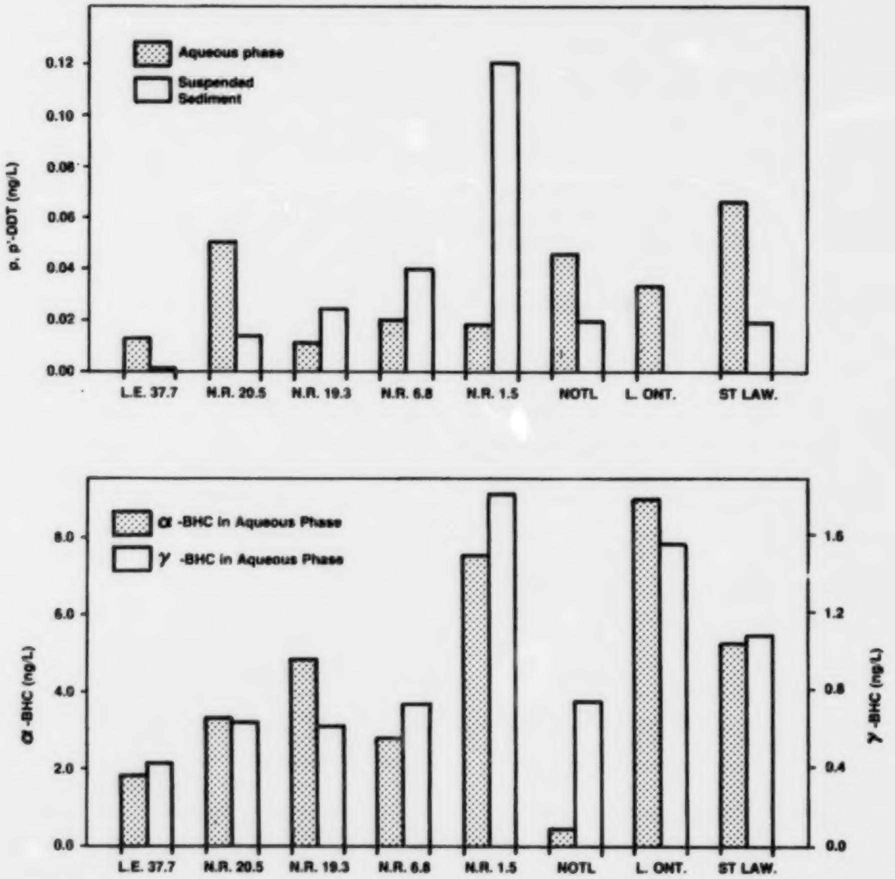

**Figure 35.** Concentrations of DDT, and α- and γ-BHC in aqueous and suspended particulate phases at different sites between Lake Erie and the St. Lawrence River. L.E. 37.7 – Lake Erie 37.7 mi upstream from NOTL; N.R. 6.8 – Niagara River 6.8 mi upstream from NOTL; NOTL – Niagara-on-the-Lake; L.Ont. – Lake Ontario; ST. LAW. – St. Lawrence River (after McCrea *et al.*, 1983).

Shifts in particulate-aqueous phase partitioning are likely to occur with time because of changes in suspended particulate load. The suspended particulate concentration at Niagara-on-the-Lake was a mean of 2.8 mg/L under ice from January to March 1981, but rose to a mean of 8.0 mg/L (3.1 to 23.2 mg/L) from May to December, probably related to the ice cover on Lake Erie which reduces suspended particulate input to the Niagara River. Thus, aqueous phase transport is probably important in the winter months. At polluted sites, meaningful predictions of organic chemical partitioning and thus the role of particulates in their transport require well-documented knowledge of suspended load variations with season.

Kuntz and Warry (1983) calculated the sediment-water partition coefficients for some chemicals in the Niagara River (Table 17). The soluble mass was the difference between the whole water mass and suspended particulate mass of specific chemicals. Reasonable agreement was found with published information based on laboratory measurements of octanol-water partition coefficients. From analyses of particulates settling in Lake Ontario, Oliver and Charlton (1984) made estimates of sediment water partition coefficients for chlorobenzenes and also found reasonable agreement with predicted values for the more hydrophobic chemicals (Table 18). However, the field-determined $K_{OC}$'s are considerably higher than the predicted values for the more soluble compounds, but this may be explained by the largely biotic origin of the particulates caught in the sediment traps. The "apparent" partitioning thus may involve a bioconcentration factor (Oliver and Nicol, 1984).

If the partition coefficient (the log of the ratio of the concentration in particulates to the concentration in solu-

**Table 17. Calculated and Reference Partition Coefficients for Organochlorine Compounds in the Niagara River**

| Chemical | Sediment concentration (ng/g) | Total water concentration (pg/g) | Log sediment/water partition coefficient | Log octanol/water partition coefficient |
|---|---|---|---|---|
| Total PCBs | 500 | 11.0 | 4.9 | 4.0–6.1 |
| HCB | 49 | 0.5 | 5.7 | 5.5 |
| $\gamma$-BHC | 1 | 1.8 | 2.8 | 3.5 |

After Kuntz and Warry (1983).

tion) was dependent only on the solubility or related properties of organic chemicals, and if equilibrium was always attained between the particulate and aqueous phases, then the mass of a chemical transported on the particulate phase should be readily predicted (Table 19; Fig. 36). For example, the Niagara River has a mean annual suspended particulate load of 8.4 mg/L. Given this suspended particulate concentration, some 50% or greater of toxic chemicals and elements with partition coefficients larger than $10^5$ should be transported in the particulate phase. The mass transported by the particulate phase increases with increasing particulate concentration and with increasing partition coefficient.

**Table 18. Some Log $K_{oc}$ Values for Settling Particulates Compared with Calculated Values**

| Chemical | Log $K_{oc}$ | Log $K_{oc}$* |
|---|---|---|
| HCB | 5.8 | 5.09 |
| 1,2,4,5-TeCB | 4.77 | 4.12 |
| 1,3,5-TCB | 4.96 | 3.76 |
| 1,4-DCB | 4.57 | 2.99 |

*Based on octanol-water partition coefficient.

After Oliver and Charlton (1984).

**Table 19. Percent of Contaminant in the Particulate Fraction (if controlled solely by partition coefficient and concentration of suspended solids)**

| Suspended solids concentration (mg/L) | $K_d$ (partition coefficient) $10^7$ | $10^6$ | $10^5$ | $10^4$ | $10^3$ | $10^2$ |
|---|---|---|---|---|---|---|
| | (percent in particulate fraction) | | | | | |
| 1000 | 100[2] | 100 | 100 | 91 | 50 | 9 |
| 500 | 100 | 100 | 98 | 85 | 33 | 5 |
| 100 | 100 | 100 | 91 | 50 | 9 | 1 |
| 50 | 100 | 98 | 85 | 33 | 5 | 0[1] |
| 30 | 100 | 97 | 75 | 25 | 3 | 0 |
| 10 | 100 | 91 | 50 | 10 | 1 | 0 |
| 5 | 98 | 85 | 33 | 9 | 0 | 0 |
| 1 | 91 | 50 | 10 | 5 | 0 | 0 |

[1] Zero (0) means <1%; assuming that all natural waters contain some finite amount of suspended solids, there will always be a finite amount of partitioning.

[2] 100% means >99%; assuming that an equilibrium is established. Even for the most insoluble compounds there will always be some finite amount in solution.

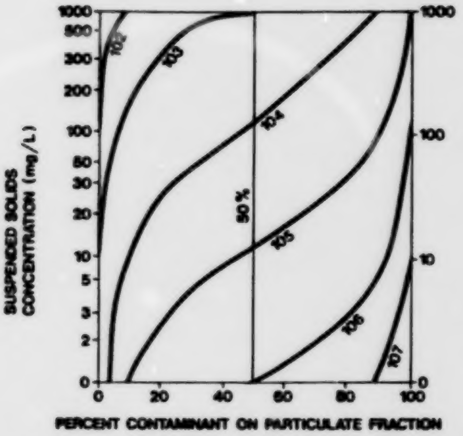

**Figure 36.** Relationship between concentration of suspended particulates and percent of contaminant transported in the suspended particulate phase (assuming no change in $K_p$ with concentration of particulates and no change in particulate organic content).

### *Particulate Phase Loads in the Niagara River*

Media concentrations of chemicals have been used along with suspended particulate concentrations and discharge to calculate the respective particulate-bound and soluble chemical loads from the Niagara River to Lake Ontario.

As noted earlier, much of the particulate toxic metal load, in most cases 60% or greater, is in a non-bioavailable form. The bioavailable fraction is that sorbed to particulates or to various degrees reversibly or irreversibly fixed in Mn and Fe oxides or as carbonates. It is important to estimate this fraction of the toxic metal load which is transported as a bioavailable particulate phase. A 0.5 *N* HCl extraction does not remove organic phases which could be bioavailable to detrivores, so that for some metals the total bioavailable fraction could be higher than quoted here. The total mean annual suspended particulate load of the Niagara River is in the order of 2 million metric tons. The total toxic metal load of the Niagara River is in the hundreds of metric tons per year (Table 20). The percentage of the

**Table 20. Percent Particulate-Transported Toxic Metals to Lake Ontario by the Niagara River in 1982**

| Element | Total load (metric tons/yr) | Total in suspended sediment (metric tons/yr) | Percent of total in suspended sediment (%) | Percent extractable* in sediment of total (%) |
|---|---|---|---|---|
| Cd | <200 | 10 | $\overline{>}5$ | $\overline{>}2$ |
| Pb | 200 | 197 | 98 | 54 |
| Cr | 410 | 275 | 69 | 10 |
| Cu | 410 | 120 | 29 | 15 |
| Zn | 610 | 673 | >100 | 59 |
| Ni | 200 | 154 | 77 | 14 |

*Extractable by 0.5 *N* HCl.

After Kuntz (1984).

total toxic metal load in suspended particulates varies from 29% to almost 100%. In addition, the easily extractable particulate phase varies from 10% to 59% of the total particulate phase. Thus, the readily bioavailable, particulate-associated Pb transported by the Niagara River is some 100 metric tons. These quantities are far greater than the total particulate or even total loads of toxic organics transported by the river.

The total quantity of toxic organic chemicals transported by the Niagara River is far less than that of toxic metals. For the highly partitioned compounds, changes in total load over a three-year period (Table 21) may be related to higher mean suspended particulate loads in 1982 and 1980 versus 1981 (10.0 versus 6.9 mg/L). Kuntz and Warry (1983) calculated the percent of organic chemicals transported by particulates in the Niagara River over the period 1979-1981 (Table 22). The variations in the transport phase of organic chemicals are consistent, on a gross scale, with predictions based on known physical-chemical properties for these compounds. All of the particulate-transported organic load is potentially bioavailable because it will either be present sorbed on (or excluded onto) particulate surfaces or bioconcentrated in biotic material. Isomers, for example of the chlorobenzenes, have different partitioning, and this is reflected in the percentages of different isomers transported in the particulate phase (Table 23). Most of the lower chlorinated benzenes are transported in the aqueous phase, as would be expected from their lower $K_{OW}$ values.

**Table 21. Particulate Loadings of Organic Chemicals to Lake Ontario (kg/yr)**

| Chemical | 1980 | 1981 | 1982 |
|---|---|---|---|
| Total PCBs | 780 | 464 | 655 |
| HCB | 62 | 50 | 23 |
| p,p′-DDT | 27 | 10 | 2 |
| Mirex | 8 | 3 | 13 |
| Lindane | 2 | 1 | 2 |

After Kuntz (1982).

**Table 22. Percent Particulate-Transported Organic Chemicals to Lake Ontario by the Niagara River, 1979–81**

| Chemical | Total load (kg/yr) | Total in suspended sediments (kg/yr) | Percent of total in suspended sediment |
|---|---|---|---|
| Total PCBs | 2200 | 850 | 39 |
| Total DDT | 20 | 41 | 100 |
| Mirex | 20* | 8 | 42 |
| Lindane | 400 | 2 | 1 |

*Value is spurious because of difficulty of detection of mirex in whole water samples; probably almost 100% of mirex is transported on particulates.

After Kuntz *et al.* (1982).

**Table 23. Percent Particulate-Transported Chlorobenzene Isomers to Lake Ontario by the Niagara River in 1982**

| Isomer | Total load (kg/yr) | Total in suspended sediments (kg/yr) | Percent of total in suspended sediment (%) |
|---|---|---|---|
| 1,4–Di | 987 | 2 | 1 |
| 1,2-Di | 987 | 2 | 1 |
| 1,2,4-Tri | 200 | 27 | 13 |
| 1,2,3-Tri | 200 | 2 | 1 |
| 1,2,3,4-Tetra | 200 | 27 | 13 |

After Oliver and Nicol (1982).

## ROLE OF COLLOIDAL PARTICULATES

The operational definition of the "aqueous" phase is material <0.45 μm or which passes through a high-speed centrifuge. "Aqueous" phase concentrations, according to the above definition, may thus contain "particles" <0.45 μm, perhaps with high surface area organic coatings, and colloids. Colloids tend to be the forgotten component in aquatic systems. Leppard (1983) has pointed out that there possibly is an important role for fibrillic colloidal material in the transport and bioavailability of contaminants. Yet few researchers have the facilities or the inclination to investigate this role. Even high-speed centrifugation has been applied only at a few locations. It seems that in most cases, the 0.45-μm filter or the Millipore filter in research studies are still the prime operational tools for separation of the particulate from "aqueous" phases.

Colloids are electrically charged particles with large surface areas and thus high sorptive capacities. In most freshwater aquatic ecosystems, the concentration of suspended particulates and turbulence play the most important roles in flocculation of colloids. Charges on colloids can be positive or negative and a variety of sorption-desorption reactions can occur, depending on the whole water chemistry and on competition between chemicals or ions for exchange sites. Colloids often have Mn and Fe or organic surface coatings and these phases are greater accumulators of pollutants than the exchange process. Colloidal organics are easily biodegradable by microbial processes, so that colloids can play a significant role at the initial stage of contaminant bioaccumulation. Many of the natural colloids in river waters are humic acid polymers. By release of protons, they are negatively charged, hydrophilic, and interact with metal ions to form metal-organic complexes by ion exchange, surface adsorption or chelation. These humic colloids can represent up to 15% of sediment organic carbon and may leach metals from bottom sediments in the same fashion as occurs in soil horizons. The importance of colloidal particulates was postulated by Karickhoff *et al.* (1979), who centrifuged water samples at 10 000 rpm for up to 1 h but could not eliminate colloidally sorbed paraquat from the "aqueous" phase. Because the colloidal materials in water are often of general fulvic or humic acid composition, they contain many functional groups, such as COOH, OH, C=O, $NH_2$ and $SH_2$. Bonding to the surface of organic colloids can be by ion exchange, protonation, hydrogen bonding, van der Waals forces, coordination complexation, and hydrophobic bonding. The particle mobility measured by electrophoresis by Hart (1982) may be related to microscopic colloidal surfaces precipitated on various particulate substrates.

In 1982, a NATO conference (Leppard, 1983) held to discuss speciation of metals in natural waters identified a need for greater studies of the role of colloids (in particular fibrillic material of algal origin) in the transport and bioavailability of toxic metals and organic chemicals. Little hard information exists on the actual role of colloids in transport and bioavailability of toxic contaminants. An important point (Leppard, 1983) is that when biological effects of metals are studied in laboratory tests or artificial field enclosures such as limnocorrals, respeciation of the metals must also be measured because the effects may not be the result of the original metal added but rather of the metal in a respeciated form. Another related, little understood but critical question is the ability of the organisms themselves to influence by excretions the speciation of trace metals in their immediate vicinity, for example, as plant roots are known to do in soils. Colloids have been largely disregarded by aquatic scientists because of difficulties in separating and analyzing them, and sophisticated techniques need to be developed to measure metal species in natural waters. At present, the intermediate class of colloidal substances that fall between the operationally defined "particulate" and "soluble" phases has never been adequately investigated in rivers and lakes. Burnison and Leppard (1983) found that fibrils (colloidal organic ribbons of some 0.005-μm diameter with lengths of some 0.5 μm) could be present in certain lakes at concentrations of up to 7 mg/L or as high as the suspended particulate load in many contaminated waterways. Burnison and Leppard (1983) have developed a filtration technique for separation of sufficient fibrils (Fig. 37) so that measurements can be made of toxic metal and perhaps eventually toxic organic chemical concentrations in this medium. Using such a separation

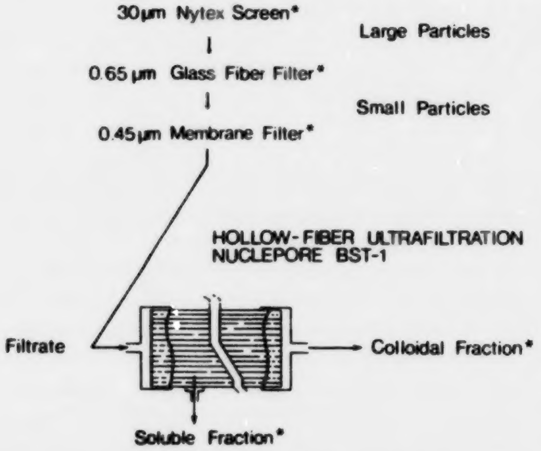

**Figure 37.** Isolation of colloidal fibrils from lake water by physical separation, observed by transmission electron microscopy (after Burnison and Leppard, 1983).

procedure, they found that the <0.45-μm particulate fraction collected by Hollow Fiber Ultrafiltration (>50 000 molecular weight) consisted of colloids and very small bacteria, and fibrils in great abundance. The fraction could be flocculated and pelletized. The soluble fraction, which contained <50 000 molecular weight material, could be flocculated but could not be centrifuged out and was not considered a significant "particulate" fraction.

Toxic metal speciation in water is strongly affected by colloid chemistry. The main impetus for metal speciation studies was the discovery of natural methylation of Hg in aquatic systems some 15 years ago. Since then there have been major advances in analytical capability, perhaps the most recent and powerful of which is the gas chromatographic/atomic absorption technique used to study alkylated lead and tin. Only a limited number of such systems, for example a programmable Perkin-Elmer 4000 Atomic Absorption combined with a Hewlett Packard 5880A Series Gas Chromatographic, exist for analyses of environmental samples. The major purpose of species analyses in various media is to relate exposure to toxicity. Although analytical chemistry has reduced toxic metal detection limits to low parts per trillion levels, toxicity testing is still commonly based on total metal concentrations and on acute toxicity. Total metal concentrations in "water" are usually in the range of 10 ppb (Cu, Ni, Zn, Pb), 1 ppb (Cd, Hg), or less. Acute toxicity tests employ much higher concentrations. If metal species were to be determined at such low total metal concentrations, the species concentrations would be in the parts per trillion range. Toxicities at such extreme low metal concentrations are unquantified and may, in fact, be unquantifiable. Ionic metal toxicities can be reduced by colloidal organics such as exudations from algae. Alternatively, toxicities for metals that occur in parts per trillion levels as organometallics (Hg, Pb, As, Sn) are often higher than for the free ionic metal (Chau and Wong, 1981). Batley (1983) lists ways of determining small-particle metal speciation, as follows:

(a) *Chemical modelling*:
Usually restricted to artificial colloid-free systems because of incomplete knowledge of all interactions if these are present.

(b) *Experimental separation techniques*:
Included are ion specific electrodes that respond only to free metals; physical size fractionation schemes using ultracentrifuges or Sephadex columns which separate various colloids with molecular weights between 500 and 300 000 and which can then be analyzed for metals and organic carbon.

(c) *Dialysis techniques*:
For very low molecular weight size fractions.

(d) *Solvent extraction*:
To remove organically complexed metals.

(e) *High pressure liquid chromatography*

(f) *Chelating resin columns*

(g) *Electrodeposition techniques*:
Such as potentiometric or anodic stripping.

(h) *UV light*:
To decompose only organic colloids.

Thus there are a variety of techniques for separation of "water" into size fractions and/or species in the colloidal and particulate size ranges which pass through 0.45-μm filters and centrifuges (Batley and Florence, 1976; Hart and Davies, 1977; Figura and McDuffie, 1980). Chelating resins have been used to separate ionic and colloidal metal species and have proven that much of the Cu, Pb and Cd in natural waters are in colloidal fractions. It is thus clear that significant amounts of some toxic metals are present in natural waters in colloidally associated forms. Whether these can be defined as "particulate" forms is an operational choice. However, the colloidal role in transport, burial and bioavailability should not fall between the "soluble" or whole water interests of chemists, and the suspended particulate interests of biologists and geochemists.

## ROLE OF SURFACE MICRO-LAYERS

Toxic organic chemicals are associated with waterborne particulates primarily because they are hydrophobic and try to locate at water and other media boundaries. One such boundary is the water-air interface. Surface layers are

**Table 24. Maximum Concentrations of Some Chlorinated Hydrocarbons in Three Compartments of the Niagara River**

| Chemical | Maximum concentration | | |
|---|---|---|---|
| | Micro-layer (ng/L) | Subsurface water (ng/L) | Suspended sediment (ng/g) |
| Total PCBs | 57 | 39 | 310 |
| Heptachlor epoxide | 23 | 0 | 0 |
| α-Endosulfan | 20 | 0 | 14 |
| Lindane (γ-BHC) | 0 | 0.9 | 0 |
| HCB | 0 | 0 | 36 |

After Maguire *et al.* (1983).

enriched in lipids and thus preferentially solubilize organic chemicals. Surface micro-layers are being increasingly analyzed for toxic organic chemicals. To varying degrees micro-layers may contain biotic and abiotic particulates. A boat-mounted surface layer sampling device has recently been developed by the National Water Research Institute to obtain large volumes of surface slicks which can be processed in the APLE or by similar procedures and an assessment made of the role of surface layers in contaminant transport and bioavailability. Maguire *et al*. (1983) sampled micro-layers, subsurface water, and suspended particulates in the Niagara River (Table 24). Turbulence affects the values and concentrations must be taken as an instantaneous estimate. Although these data only show interesting concentration differences for PCBs, measurable concentrations of heptachlor epoxide (maximum concentration 22.6 ng/L) were also found in the micro-layer. It is unlikely that the micro-layer is a major transport medium, but the presence of biotic particulates in the layer may play an important role in contaminant bioavailability.

# Burial of Toxic Metals and Organics

The use of sediment cores to study historical metal inputs to lakes, rivers and reservoirs is well documented in Förstner and Wittmann (1981). Data from the major rivers in the Federal Republic of Germany show the major role of river bottom sediments as the ultimate sink for many toxic metals (Fig. 38). Zinc pollution from an urbanized area was obvious in both coarse and fine particles in river bottom sediments (Fig. 39). In river systems, the concentration of contaminants in bottom sediments can be used to detect major sources of toxic metal input. The relative degree of anthropogenic pollution can also be assessed, although a variety of variables including particle size and organic content must be taken into account by techniques such as quartz correction factors, element ratios, and the separation and analyses of uniform particle sizes. The disposal of dredge spoil on land or especially if released into other parts of a river-lake system, in nearby seas, or oceans becomes a question of potential bioavailability of bottom sediment-associated contaminants.

Bottom sediments from several of the major rivers in Europe have been analyzed by selective extraction procedures (Calmano and Förstner, 1983) (Fig. 40) because this provides valuable information on the potential bioavailability of toxic metals. These data suggest that in river bottom sediments, the surplus of toxic metals introduced into aquatic ecosystems from anthropogenic sources usually exist in relatively unstable chemical forms. As mentioned earlier, the most important accumulative phase for trace metals is the easily reducible fraction which is best removed by acidified hydroxylamine. However, toxic metals in bottom sediments occur in a variety of phases. Förstner (1982) provides a table of the major accumulative phases for toxic metals in bottom sediments and the processes by which these metals are held in these phases (Table 25). In Lake Constance, for example, most of the zinc is deposited primarily in the carbonate fraction (Förstner and Wittman, 1981) (Fig. 41).

Particles are not limited to the material that passes a 2-mm sieve. An alternative approach to show mass transport and deposition phases for toxic metals is the use of density fractionation. Dossis and Warren (1980) separated out a series of density fractions in bottom sediments from the Spencer Gulf of South Australia. Zinc concentration was the greatest in the fractions with the least density (organic debris) and the greatest density (heavy minerals). The greatest weight percent was always in quartz grains. The major mass of the zinc was in three different "type" fractions (Fig. 42), namely "conglomerates" of clays and carbonates, shell fragments, and heavy minerals.

**Table 25. Mechanisms of Metal Enrichment in Lacustrine Sediments**

| Mechanisms | Rock debris, solid waste material, including detrital organics | Metal -hydroxide -carbonate -sulphide -phosphate | Reactive organic substances | Hydrous Fe-oxides (autochthonous) | Calcium carbonate |
|---|---|---|---|---|---|
| Inert bonding | xxx | | (x) | | |
| Adsorption | (x) | | | (x) | |
| Ion exchange | x | (x) | x | x | (x) |
| Coprecipitation | | | | xxx | x |
| Precipitation | C | xx | | C | C |
| Flocculation | | | xx | | |

xxx – Most significant process.
x – Least significant process.
(x) – Possibly significant process.

C – Substrate for "coatings."

After Förstner (1982).

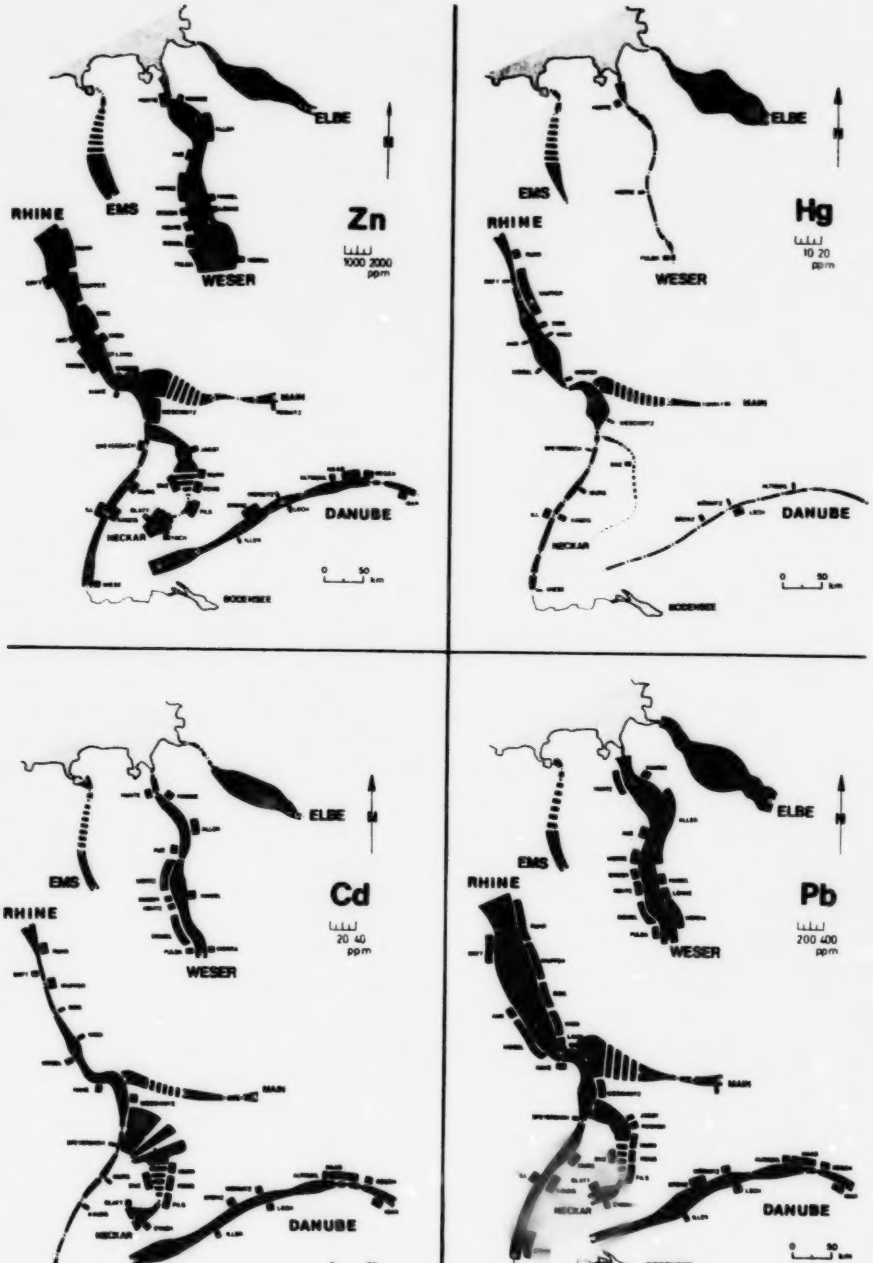
ELBE
EMS
WESER
RHINE
MAIN
NECKAR
DANUBE
BODENSEE
Zn
1000 2000 ppm
Hg
10 20 ppm
Cd
20 40 ppm
Pb
200 400 ppm
N
0 50 km

Figure 38. Heavy metals in the pelitic fraction of sediments from major rivers in the Federal Republic of Germany (after Förstner and Müller, 1974).

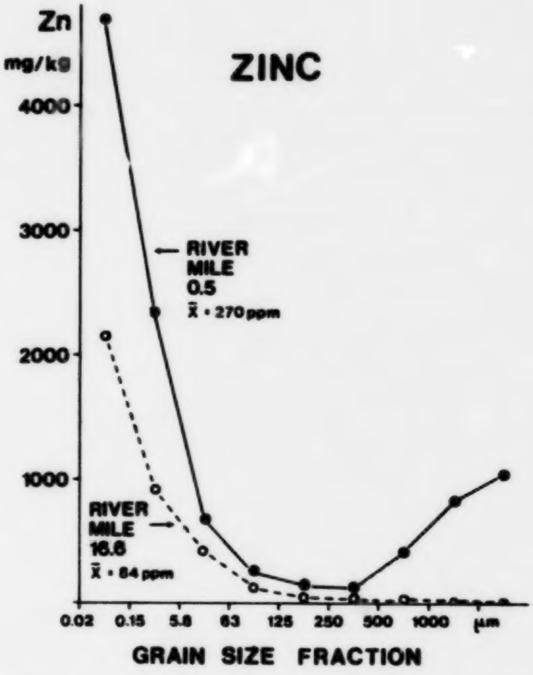

Figure 39. Grain size distribution of zinc in two sediment samples from Saddle River, upstream (mile 16.6) and downstream (mile 0.5) from an urbanized area of Lodi, New Jersey (after Wilber and Hunter, 1979).

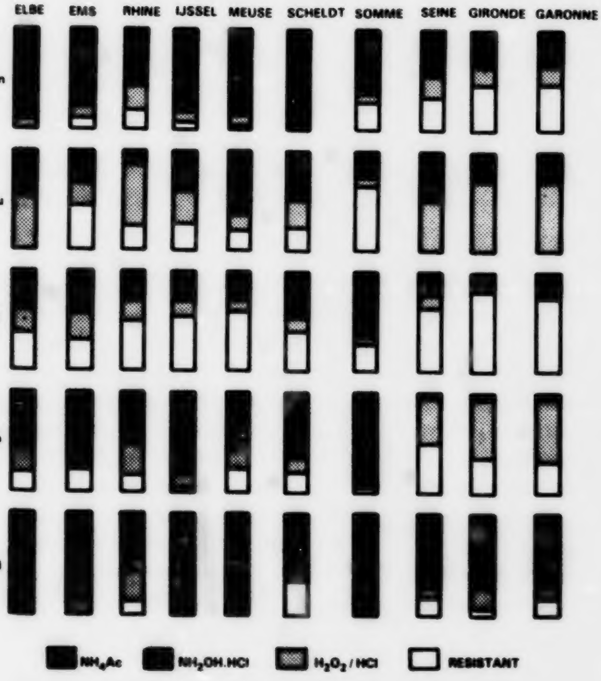

Figure 40. Speciation of trace metals in sediment samples from ten rivers in Central and Western Europe (after Calmano and Förstner, 1983).

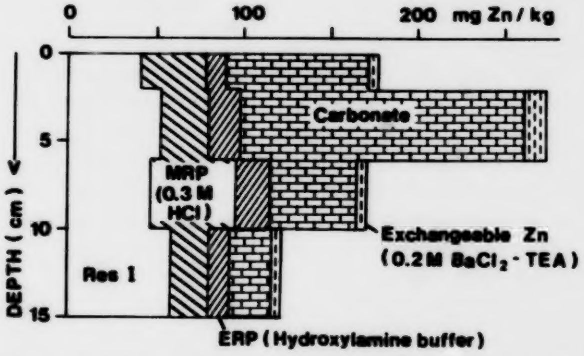

Figure 41. Depth profile of zinc and its chemical associations in a sediment core from central Lake Constance (after Förstner and Wittmann, 1981).

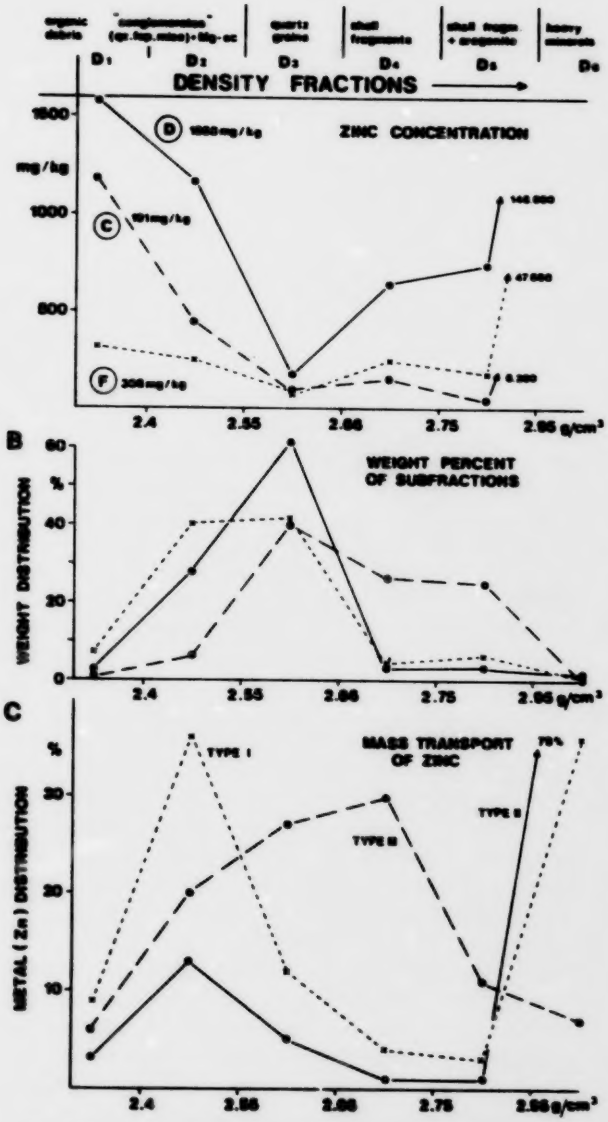

Figure 42. Density distribution of solid phases and zinc concentrations in three sediment samples from Spencer Gulf, South Australia (after Dossis and Warren, 1980).

## MERCURY IN BOTTOM SEDIMENTS OF THE WABIGOON/ENGLISH RIVER SYSTEM

The bottom sediments of the Wabigoon River system (Fig. 43) downstream from Dryden contain most of the mercury released by a chloro-alkali plant operated at Dryden for a 12-year period (Allan *et al.*, 1984). Background concentrations of Hg in the bottom sediments of off-system lakes are in the order of 100 to 200 ppb, as are the sediments of Wabigoon Lake immediately above Dryden. For some distance downstream from Dryden, the top 5 cm of bottom sediment exceeds a concentration of 1 ppm total Hg (Fig. 44). The concentration distributions of mercury with depth in bottom sediment cores from Clay

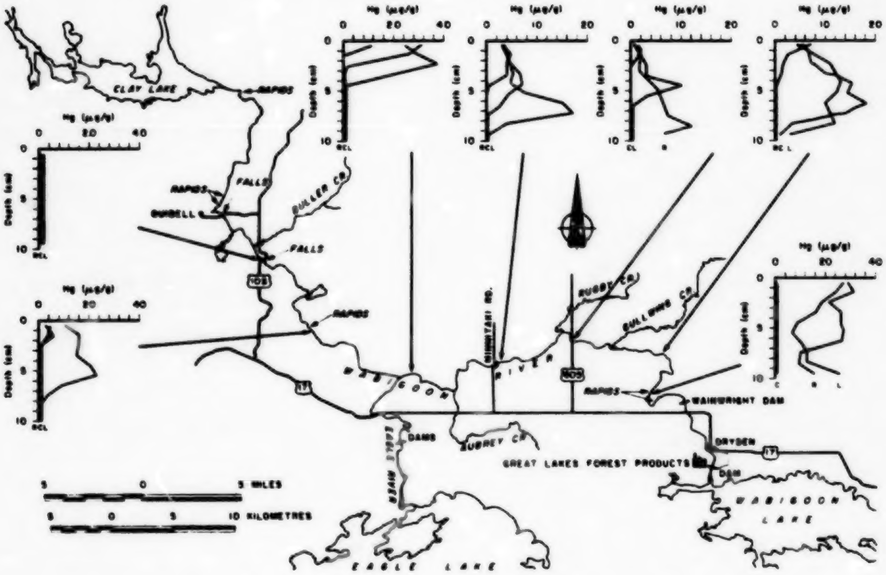
Hg (µg/g)
0
20
40
10
Depth (cm)
5
CLAY LAKE
RAPIDS
FALLS
BULLER CR.
GUDBELL
105
WABIGOON
RIVER
GUNNEY CR.
SHELLING CR.
609
17
WAINWRIGHT DAM
DRYDEN
DAMS
GREAT LAKES FOREST PRODUCTS
DAM
AUBREY CR.
EAGLE RIVER
WABIGOON LAKE
EAGLE LAKE
5 0 5 MILES
5 0 5 10 KILOMETRES

Figure 43. Mercury in Wabigoon River bottom sediment cores (after Parks *et al.*, 1984).

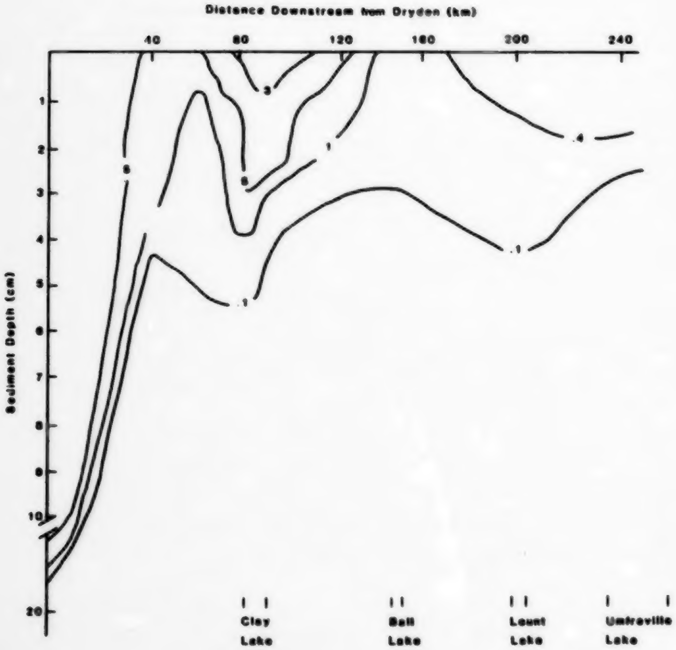

Figure 44. Approximate mercury concentration contours (µg/g) for surficial sediments, Wabigoon/English River system, 1980. Samples obtained by Phelger Corer (after Parks *et al.*, 1984).

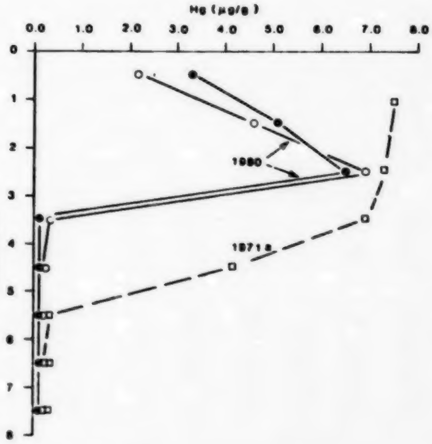

Figure 45. Variation in mercury concentration with depth, Clay Lake, western basin 1971 and 1980 (after Parks *et al.*, 1984).

Lake, the first large settling basin some 75 km downstream from Dryden, show that the high surficial values of 1971 were found at a depth of some 3 cm in 1980 (Fig. 45). However, note that upstream resuspension of contaminated sediments maintains the surface sediment total Hg concentrations in Clay Lake at the high level of 2 to 3 ppm even in 1980.

## TOXIC METALS IN SURFICIAL SEDIMENTS OF THE GREAT LAKES

Distributions of many toxic metals in surficial bottom sediments of the Laurentian Great Lakes are found in Thomas and Mudroch (1979). The distributions have been contoured for all five Great Lakes. Two main patterns involving geological and anthropogenic inputs can be identified. The distribution of Cd (Fig. 46) indicates greater anthropogenic inputs of this metal to Lake Erie and downstream Lake Ontario. A similar pattern is followed by Hg, Zn and Pb. The other pattern occurs for metals such as Cu (Fig. 47), which in Lake Superior and Georgian Bay is of largely natural geological origin and related to erosion of mineralized bedrock. The pattern for Cu is also followed by Cr and Ni, probably for the same reasons.

## TOXIC METALS IN BOTTOM SEDIMENTS OF THE NIAGARA RIVER AND LAKE ONTARIO

A USBM-54 sampler was used to collect the top 3 cm of bottom sediment in the Niagara River. The sample is protected by a bucket to prevent washout. The bottom sediments were primarily sandy. Both Lake Erie and Lake Ontario were sites of former mercury pollution from upstream chloro-alkali plants. Concentrations of Hg in bottom sediments (Kuntz, 1984) (Fig. 48a) were usually low and in most of the samples did not exceed the dredge spoil objective of 300 ppb total Hg. Except in isolated cases, the river is not a site of Hg deposition. The distribution of Hg in the bottom sediments was useful in indicating zones of the river where sources of Hg were suspected. In the upper river, there was at least a tenfold difference in bottom sediment concentrations of Hg between the U.S. and the Canadian sides of the river. The areas of high As concentrations coincided with the areas of higher Hg concentration. Concentrations for both elements dropped downstream from Niagara Falls. It remains unknown whether the upstream sites are zones of only temporary sedimentation prior to resuspension and farther downstream transport to Lake Ontario. When extractable metals (0.5 *N* HCl) were determined, for example Cd (Fig. 48b), the same general concentration distributions were found.

Lake Ontario has three sedimentation basins, namely from west to east, the Niagara, Mississauga and Rochester basins, with total sedimentation rates of 0.75, 0.70 and 2.59 million tonnes per annum, respectively (Fig. 49). Most studies of contaminant burial have been conducted at sites near the mouth of the Niagara River or in the central Niagara Basin, because sedimentation processes are rapid there and historical records of contaminant inputs are accordingly most easily recognized. The Niagara River is the major source of suspended sediments to Lake Ontario (Fig. 49). Particulates entering Lake Ontario from the Niagara River do so as a plume (or jet) which is deflected eastwards by the Niagara Bar and eventually mixes with true Lake Ontario circulation patterns. Most of the time, the overall effect diverts the river plume along the southern shore of the lake. At the exact site where the Niagara River joins Lake Ontario, there is a relatively deep zone of scour some 22 m in depth. Outside this zone of scour lies the offshore Niagara Bar (Fig. 50a). Both the inner and outer Niagara bars are actively forming by sedimentation of particulates derived from shoreline areas west of the Niagara River. The outer bar sediments are probably of glacial origin. The main outflow of the Niagara River is to the east and northeast of the river mouth and is defined by scour channels. Some fine suspended material may be transported over the bar to the west-north-northwest.

The main zones of toxic metal (and organic chemical) burial are located on the lake bed proper at the immediate outer edge of the bar. A zone of high organic and sulphur content in bottom sediments is located here and corresponds with the area of maximum, quartz corrected, Hg concentrations in surficial bottom sediments (Sly, 1983b) (Fig. 50b). On entering the lake in the Niagara River plume, some of the particulate-bound contaminant fraction is deposited at this site. Most of the fine suspended particulates in the plume are transported farther out into Lake Ontario and deposited over a wide area. In Lake Ontario, the depth distribution of several toxic metals (Hg, Pb, Cu, Zn and Cr) in bottom sediment cores from the western basin of Lake Ontario indicated that their prime source was the Niagara River. A recent significant decrease in Hg load from the Niagara River was recorded in the cores (Fig. 51). Decreases in inputs were also recorded for other metals at this site of rapid sedimentation. The mercury distribution shows that this former site of maximum surficial sediment mercury concentration now has surface sediment concentrations less than those of surficial sediments farther out in the lake. This is an important by-product of sedimentation in the long-term recovery of polluted lakes by burial of contaminants in bottom sediments. The rapid burial of the extreme concentrations is partly compensated for by slow burial and related continued bioavailability of the contaminant at other initially less polluted sites. The presently more contaminated sediments remain well within benthic organism mixing depths, whereas the former maximum contaminant concentrations near the Niagara River mouth are now below this depth.

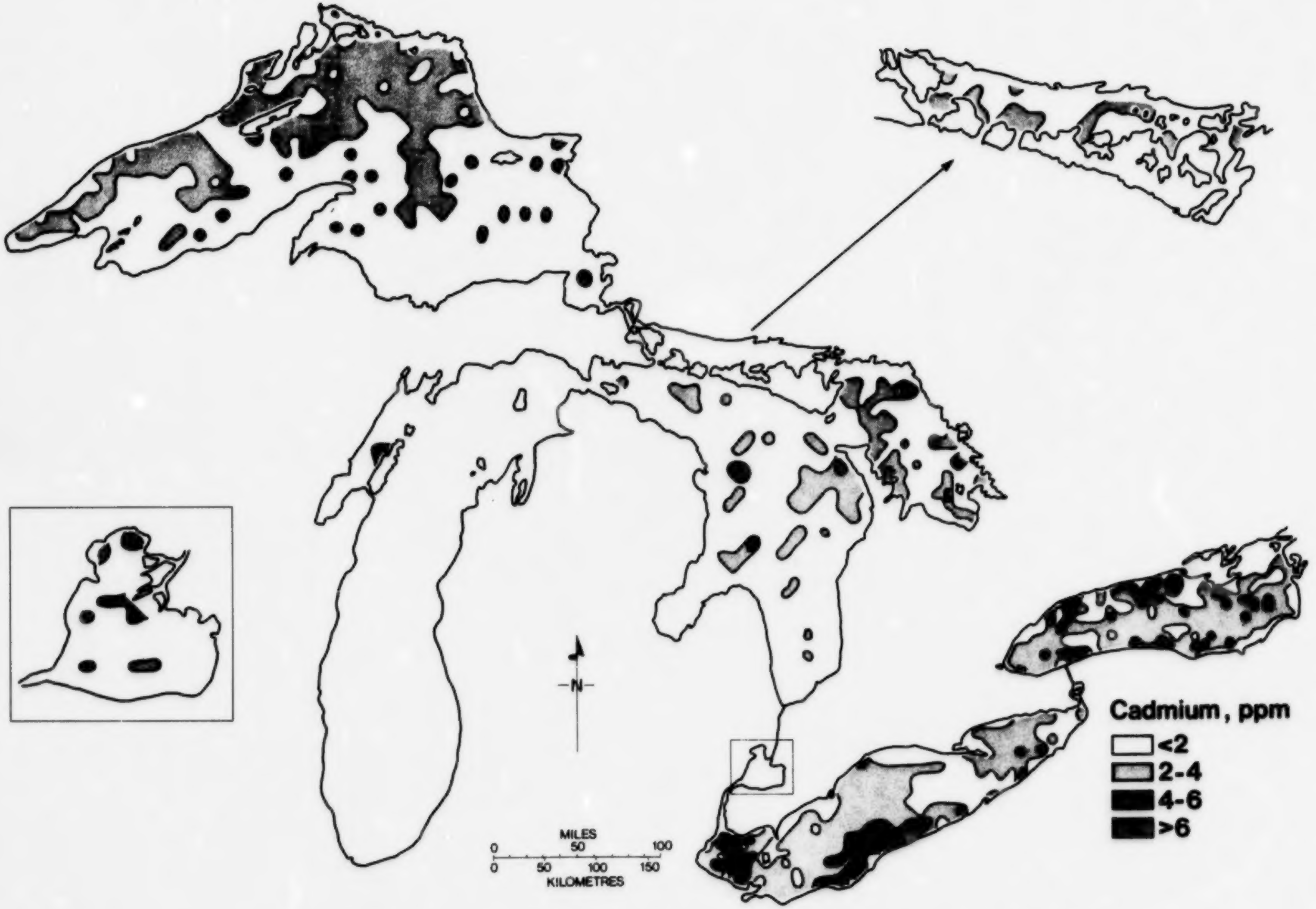
Cadmium, ppm
<2
2-4
4-6
>6
N
MILES
0
50
100
0
50
100
150
KILOMETRES

Figure 46. Distribution of cadmium in surficial bottom sediments of the Laurentian Great Lakes (after Thomas and Mudroch, 1979).

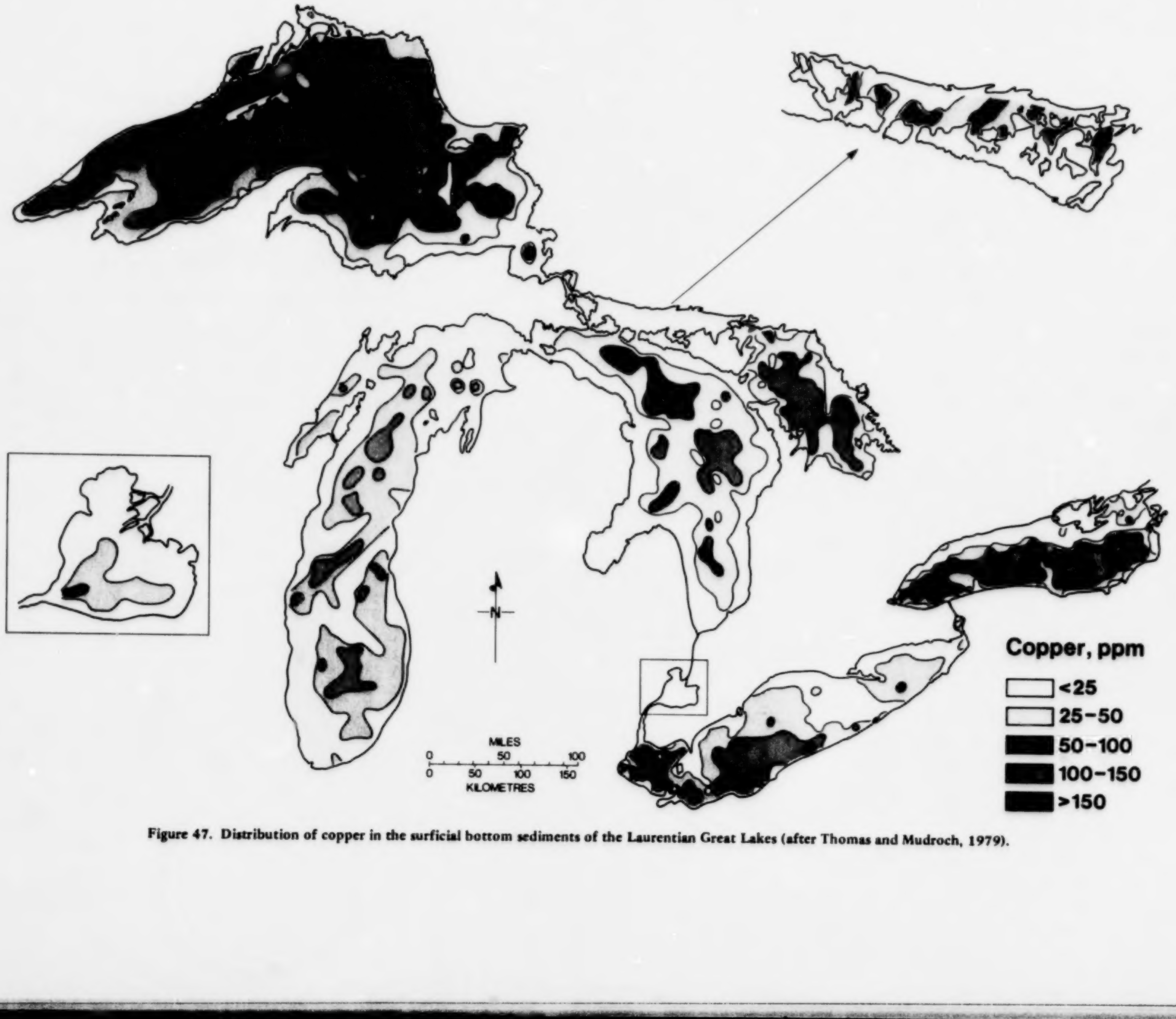
Copper, ppm
□ <25
▨ 25–50
■ 50–100
■ 100–150
■ >150
N
MILES
0
50
100
0
50
100
150
KILOMETRES

Figure 47. Distribution of copper in the surficial bottom sediments of the Laurentian Great Lakes (after Thomas and Mudroch, 1979).

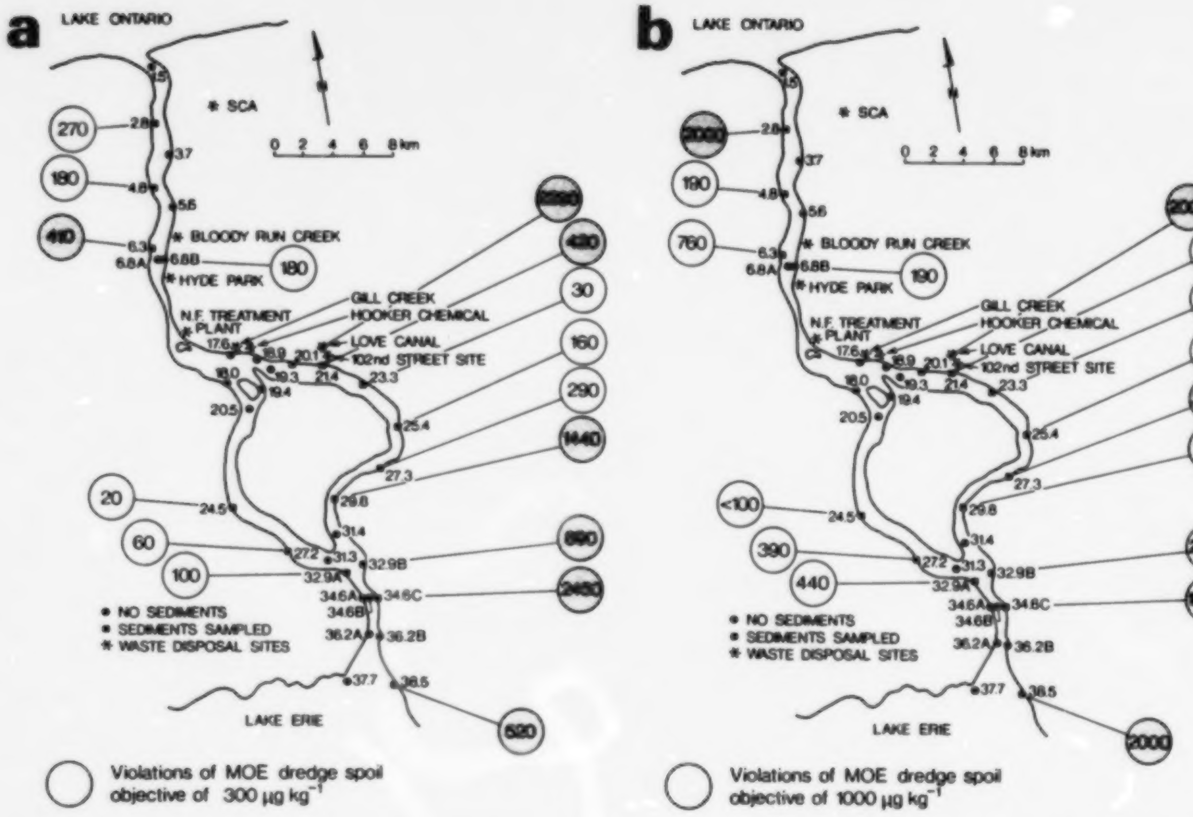
a
b
LAKE ONTARIO
SCA
0 2 4 6 8 km
N
BLOODY RUN CREEK
HYDE PARK
N.F. TREATMENT PLANT
GILL CREEK
HOOKER CHEMICAL
LOVE CANAL
102nd STREET SITE
LAKE ERIE
NO SEDIMENTS
SEDIMENTS SAMPLED
WASTE DISPOSAL SITES
270
190
410
180
2290
430
30
160
290
1440
20
60
100
890
2450
620
2000
190
760
190
2000
380
200
790
3200
1100
<100
390
440
2400
19000
2000
Violations of MOE dredge spoil objective of 300 μg kg⁻¹
Violations of MOE dredge spoil objective of 1000 μg kg⁻¹

Figure 48. Distribution of (a) total mercury (μg/kg) and (b) cadmium (0.5 *N* HCl extractable) in the surficial bottom sediments of the Niagara River, May 1981 (after Kuntz, 1981).

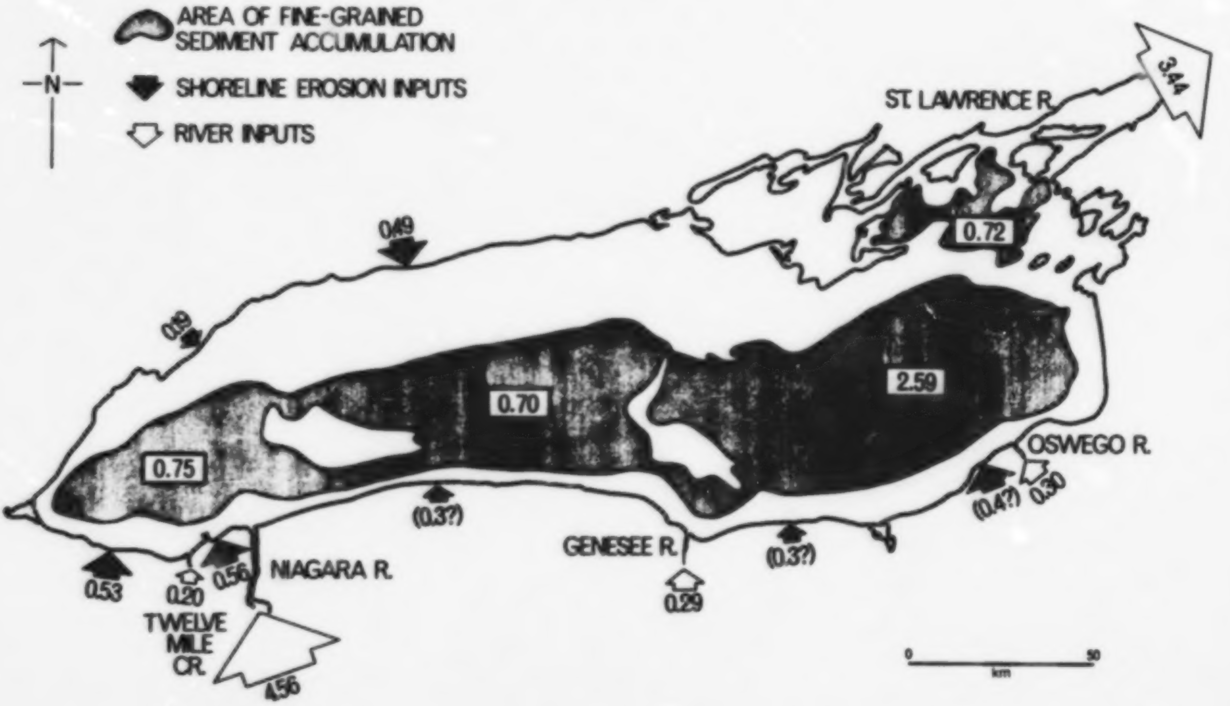
AREA OF FINE-GRAINED SEDIMENT ACCUMULATION
SHORELINE EROSION INPUTS
RIVER INPUTS
N
ST. LAWRENCE R.
3.44
0.72
0.49
0.19
0.70
2.59
0.75
OSWEGO R.
(0.4?)
0.30
(0.3?)
GENESEE R.
(0.3?)
0.29
0.53
0.20
0.56
NIAGARA R.
TWELVE MILE CR.
4.56
0
50
km

Figure 49. Sedimentation basins and sediment deposition in $10^6$ tonnes/year in Lake Ontario.

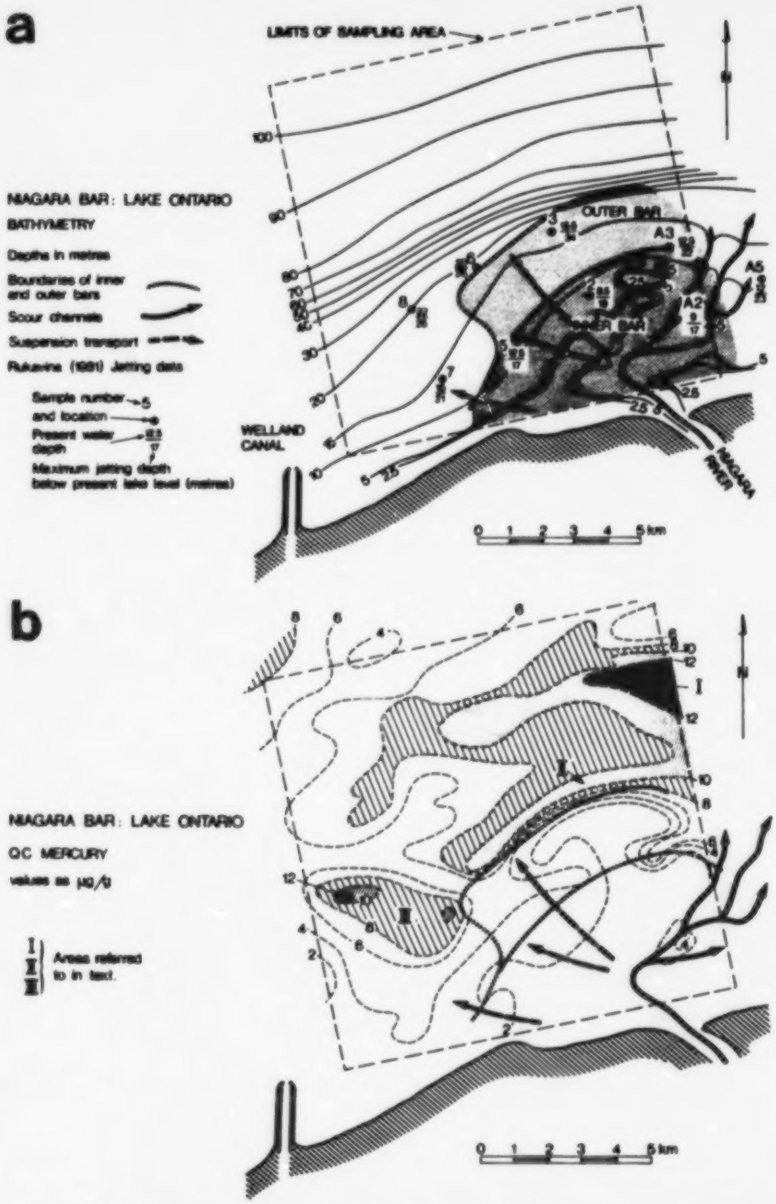
a
LIMITS OF SAMPLING AREA
N
NIAGARA BAR: LAKE ONTARIO
BATHYMETRY
Depths in metres
Boundaries of inner and outer bars
Scour channels
Suspension transport
Rukavina (1981) Jetting data
Sample number
and location
Present water depth
Maximum jetting depth below present lake level (metres)
100
90
80
70
60
50
40
30
20
10
OUTER BAR
INNER BAR
A3
A2
A5
WELLAND CANAL
NIAGARA RIVER
0 1 2 3 4 5 km
b
NIAGARA BAR: LAKE ONTARIO
QC MERCURY
values as μg/g
I
II
III
Areas referred to in text.
0 1 2 3 4 5 km

Figure 50. Bathymetry and jetting site (a) and distribution of quartz-corrected mercury (b) in Niagara River Bar, Lake Ontario (after Sly, 1983b).

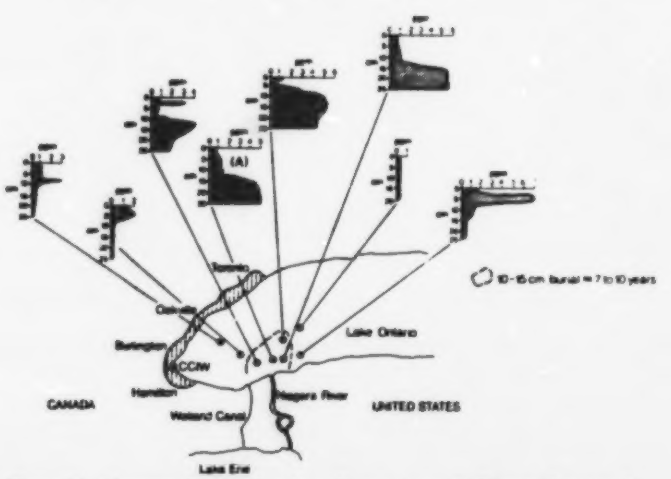

Figure 51. Mercury distribution in sediment cores. Sedimentation rate in core (A) by $^{137}$Cs is 1 cm/yr (after Mudroch, 1983).

## TOXIC ORGANICS IN SURFICIAL SEDIMENTS OF THE GREAT LAKES

The most extensive and systematic research into the distribution of toxic organics in surficial sediments has been conducted in the Laurentian Great Lakes. Distribution diagrams for several of the major contaminants such as mirex, PCBs and DDT are published for all five of the Laurentian Great Lakes. The results show that the bottom sediments of these lakes, and by extrapolation the bottom sediments of other lakes and reservoirs, are major sinks or sites of eventual burial of organic chemicals in aquatic ecosystems. The distribution patterns provide clues to zones or sites of maximum loadings and permit analyses of long-term input trends. A double, stainless steel, mini-Shipek dredge was developed by the National Water Research Institute for collection of surficial bottom sediments, but a variety of bottom sediment dredges are commercially available. The distribution of total PCBs and total DDT in Lake Michigan surficial sediments is shown in Figure 52 (Frank *et al*., 1981a). The distribution of PCBs and mirex in Lake Ontario (Fig. 53) (Thomas, 1983) was determined using the same basic 10-km surface sediment sampling grid and the Shipek dredge. The mean level of PCBs in Lake Ontario was 57 ppb. The chemical DDT and metabolites were present at a mean total concentration of 42.8 ppb. The PCB concentrations in Lake Ontario can be compared with the small areas of greater than 20 ppb in Lake Michigan. Thomas (1983) has explained the use of surficial bottom sediments to indicate the Niagara River as the source of PCB and mirex loading to Lake Ontario. The physical transport pathway of particulate-bound contaminants in Lake Ontario is characteristically traced by the PCB and mirex distributions. The present limited analyses of a few sediment samples for TCDD (tetra-chlorodibenzoparadioxin) also seem to fit the same pattern (Fig. 54). The distributions of many organic chemicals in the surficial bottom sediments of the Great Lakes have been extremely valuable in revealing the major sources of input of specific toxic organic chemicals. For example, the input of PCBs from Saginaw Bay, Michigan, to

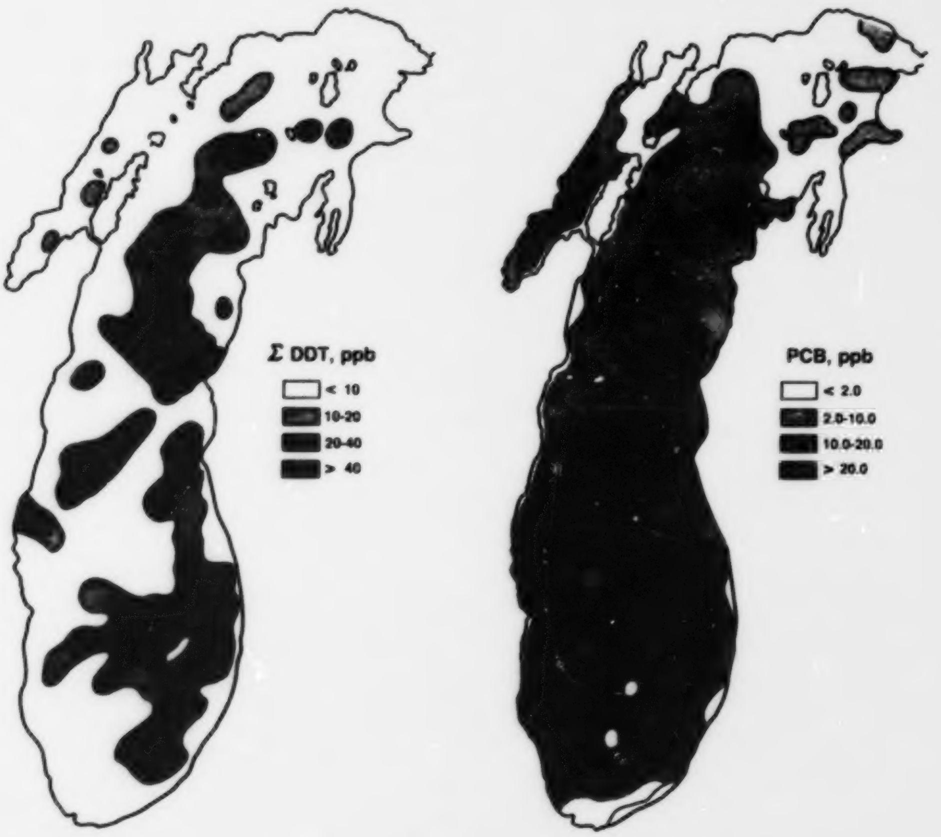

Figure 52. Distribution of total DDT and PCBs in surficial bottom sediments of Lake Michigan (0.3–3 cm) (after Frank *et al*., 1981a).

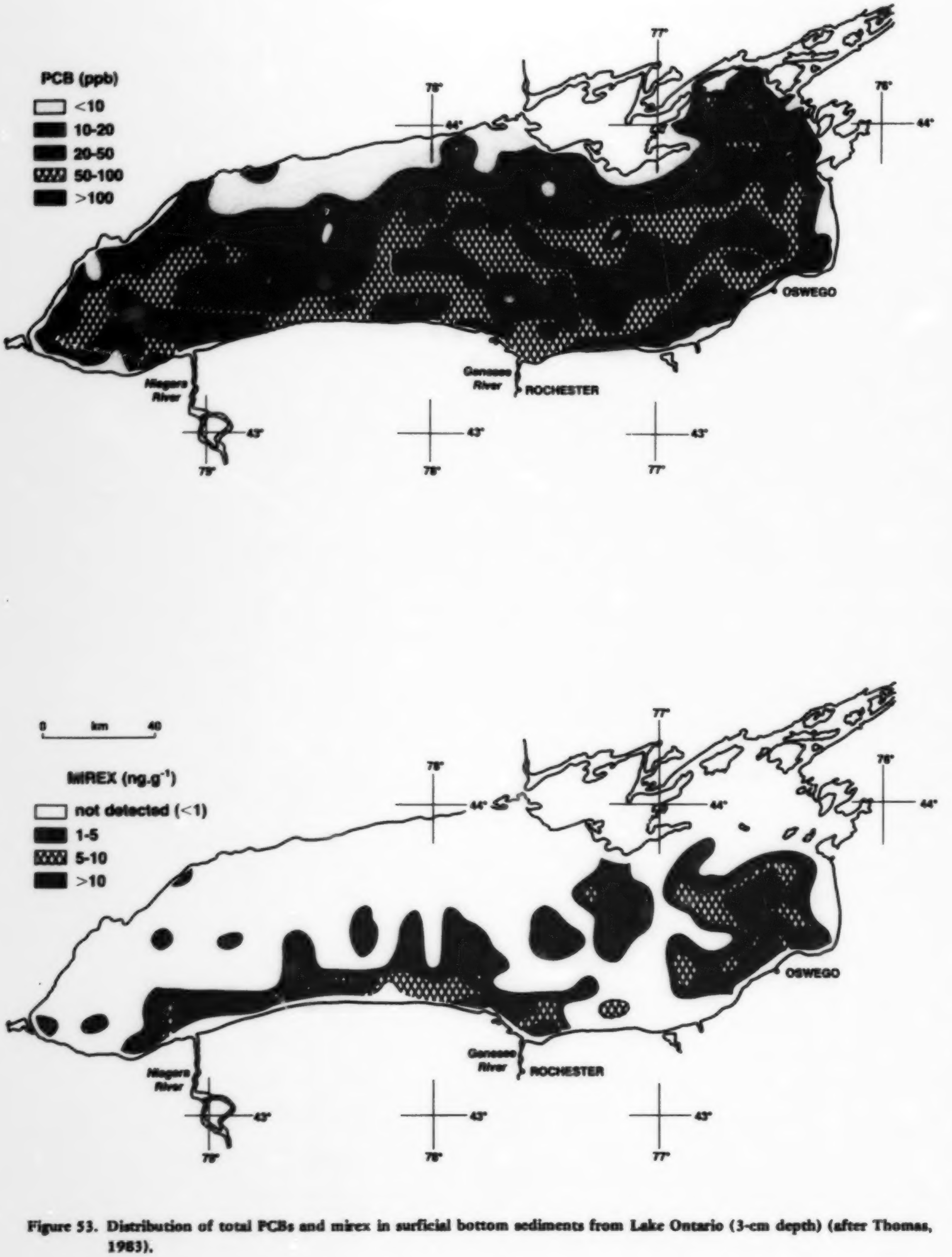
PCB (ppb)
☐ <10
■ 10-20
■ 20-50
▨ 50-100
■ >100
77°
78°
76°
44°
OSWEGO
Genesee River
ROCHESTER
Niagara River
43°
79°
0 km 40
MIREX (ng.g⁻¹)
☐ not detected (<1)
■ 1-5
▨ 5-10
■ >10

Figure 53. Distribution of total PCBs and mirex in surficial bottom sediments from Lake Ontario (3-cm depth) (after Thomas, 1983).

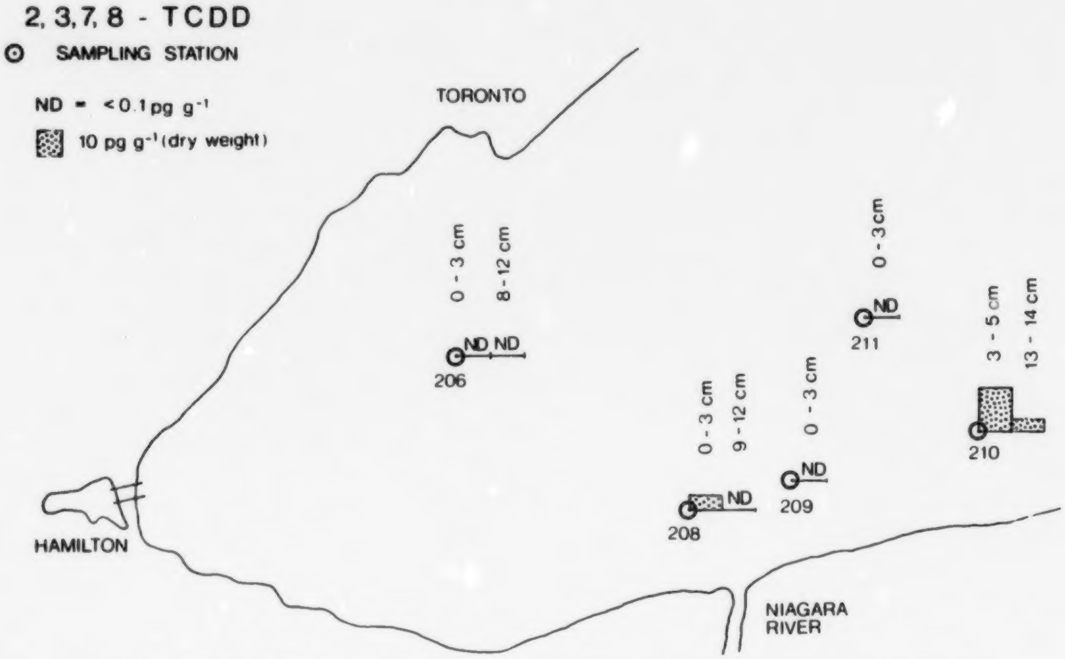
2, 3,7, 8 - TCDD
SAMPLING STATION
ND = <0.1 pg g⁻¹
10 pg g⁻¹ (dry weight)
TORONTO
HAMILTON
NIAGARA RIVER
0 - 3 cm
8 - 12 cm
ND ND
206
0 - 3 cm
9 - 12 cm
ND
208
0 - 3 cm
ND
209
0 - 3cm
ND
211
3 - 5 cm
13 - 14 cm
210

**Figure 54.** The TCDD distribution in bottom sediment cores from Lake Ontario (after Onuska *et al.*, 1983).

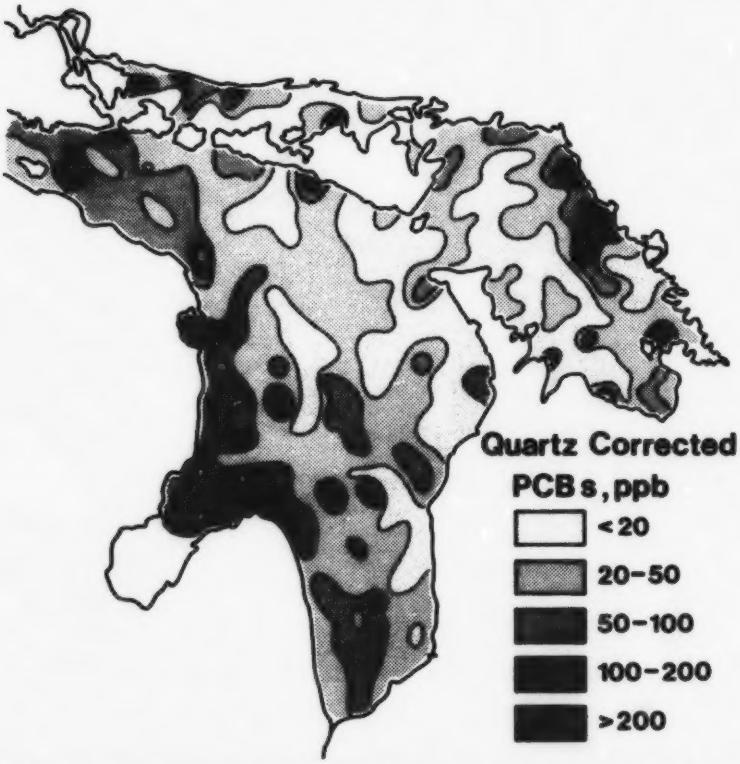
Quartz Corrected
PCBs, ppb
<20
20–50
50–100
100–200
>200

**Figure 55.** Distribution of quartz-corrected PCBs in surficial bottom sediments from Lake Huron, Georgian Bay and North Channel (0–3 cm) (after Frank *et al.*, 1979b).

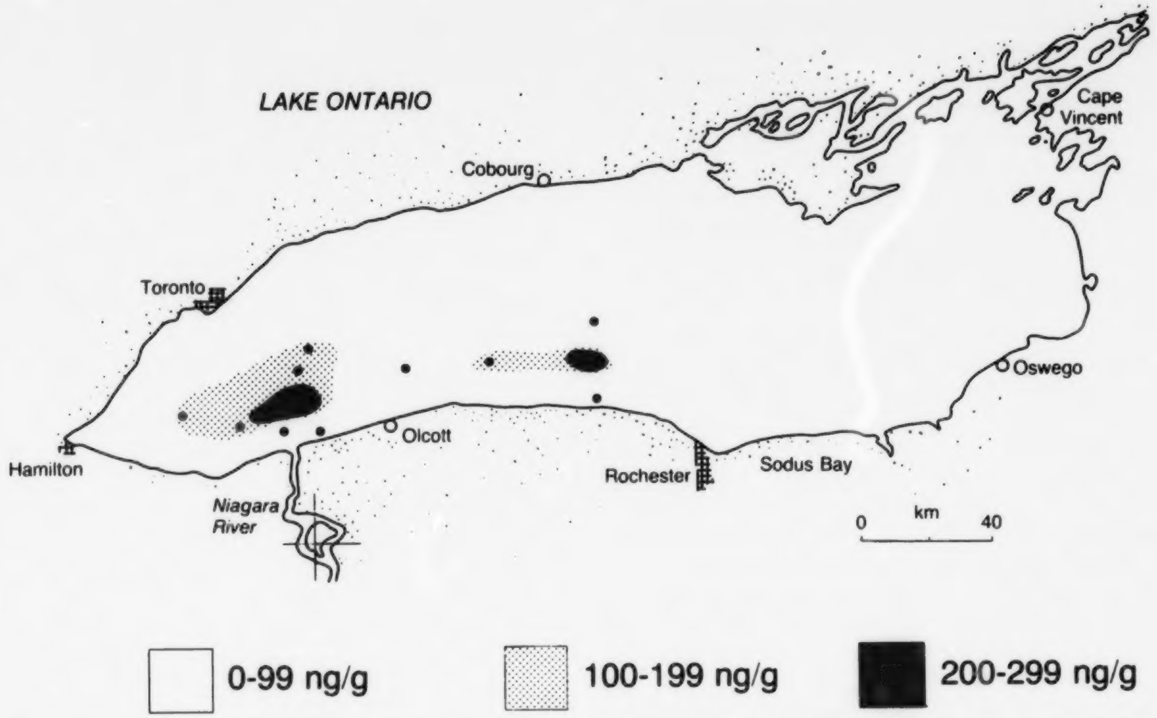
LAKE ONTARIO
Cape Vincent
Cobourg
Toronto
Oswego
Olcott
Hamilton
Rochester
Sodus Bay
Niagara River
0
km
40
0-99 ng/g
100-199 ng/g
200-299 ng/g

Figure 56. Distribution of chlorinated benzenes and toluenes in Lake Ontario bottom sediments. Concentrations are expressed in nanograms of chloro organic compounds per gram dry weight of sediment (after Kaminsky *et al.*, 1983).

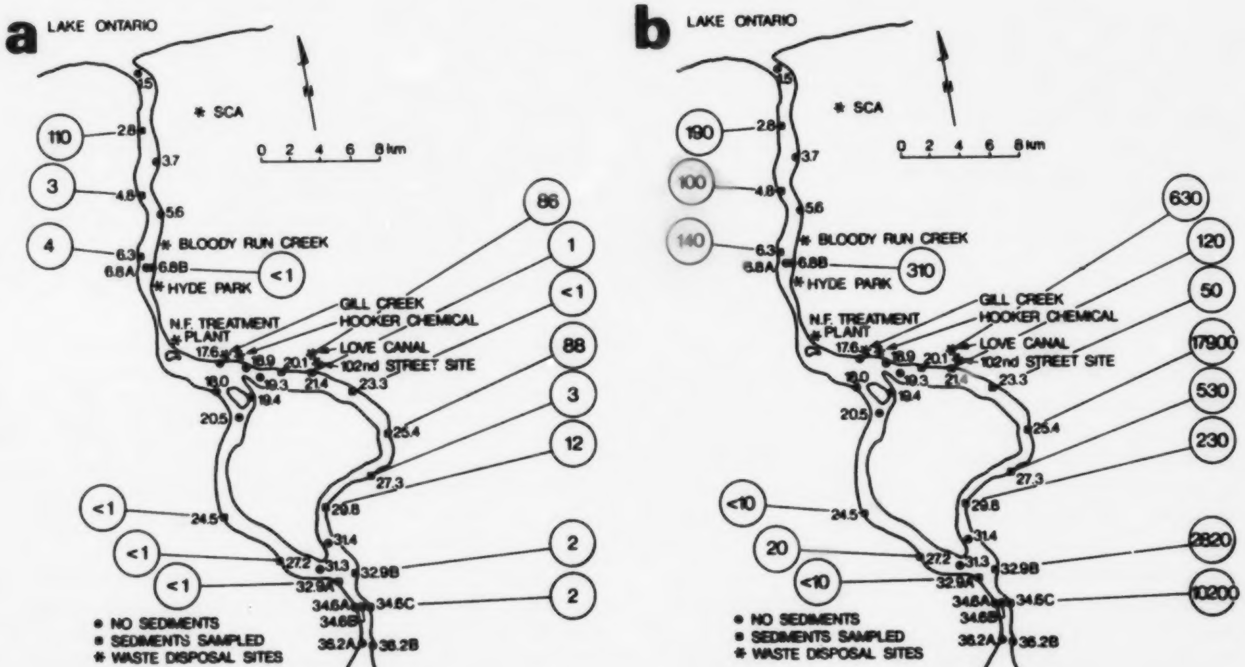
a
LAKE ONTARIO
SCA
0 2 4 6 8 km
110
3
4
<1
86
1
<1
88
3
12
<1
<1
<1
2
2
2
BLOODY RUN CREEK
HYDE PARK
N.F. TREATMENT PLANT
GILL CREEK
HOOKER CHEMICAL
LOVE CANAL
102nd STREET SITE
1.5
2.8
3.7
4.8
5.6
6.3
6.8A
6.8B
17.6
18.0
18.9
19.3
19.4
20.1
20.5
21.4
23.3
24.5
25.4
27.2
27.3
29.8
31.3
31.4
32.9A
32.9B
34.6A
34.6B
34.6C
36.2A
36.2B
37.7
38.5
NO SEDIMENTS
SEDIMENTS SAMPLED
WASTE DISPOSAL SITES
LAKE ERIE
b
LAKE ONTARIO
SCA
0 2 4 6 8 km
190
100
140
310
630
120
50
17900
530
230
<10
20
<10
2820
10200
480
BLOODY RUN CREEK
HYDE PARK
N.F. TREATMENT PLANT
GILL CREEK
HOOKER CHEMICAL
LOVE CANAL
102nd STREET SITE
NO SEDIMENTS
SEDIMENTS SAMPLED
WASTE DISPOSAL SITES
LAKE ERIE

Figure 57. Distribution of hexachlorobenzene (a) and total PCBs (b) (μg/kg) in bottom sediments of the Niagara River, May 1981 (after Kuntz, 1984).

Lake Huron, can be readily seen from the surficial bottom sediment PCB distributions, especially when the concentrations are normalized for quartz content (Frank *et al.*, 1979b) (Fig. 55). More recently in Lake Ontario, Kaminsky *et al.* (1983) used surficial bottom sediments to make a preliminary estimate of CB and CT distributions (Fig. 56). They applied the technique of using unique organic chemicals to trace sources and found that two chlorofluorinated compounds found in Lake Ontario sediments came from a source over 100 km away on the Niagara River.

## TOXIC ORGANICS IN BOTTOM SEDIMENTS OF THE NIAGARA RIVER AND LAKE ONTARIO

Surficial bottom sediments from the Niagara River have been used to detect source zones. For example, the distribution of HCB (Fig. 57) showed that the major sources were on the U.S. side of the river. However, the maximum concentration of 110 ppb was nearshore on the Canadian side downstream from Niagara Falls and remote from any immediate input. Similar patterns were found for mirex and TeCBs. The highest surficial bottom sediment concentrations of mirex (890 ppb) and TeCB (211 ppb) occurred just downstream from the main suspected source of these compounds. Polychlorinated biphenyl (Fig. 57) and DCB concentration distributions were more akin to those shown earlier for toxic metals, in that major sources were detected in the upper Niagara River on the United States side. The maximum PCB bottom sediment concentration was 17.9 ppm. The distribution of DCB showed that there was a significant input of this chemical from Lake Erie but that this load was added to from sources in the United States above Niagara Falls. It should be noted that a major input of chemicals is from the Niagara Falls Wastewater and Sewage Treatment Plant (NFWSTP) immediately downstream from the Falls, but that the high flow rate and turbulence in the Niagara Gorge prevent sedimentation in this section of the river. Once contaminants have entered Lake Ontario from the Niagara River, most of the particulates and their associated chemical load settle out near the river mouth. Only the finer particle sizes and the material in solution pass out into the lake where it interacts with lake circulation processes and particulates in the lake from other sources such as shoreline erosion or as a result of primary production. Hydrophobic/lipophillic compounds continue to be partitioned onto these particulate phases which continue to settle out in all parts of the lake.

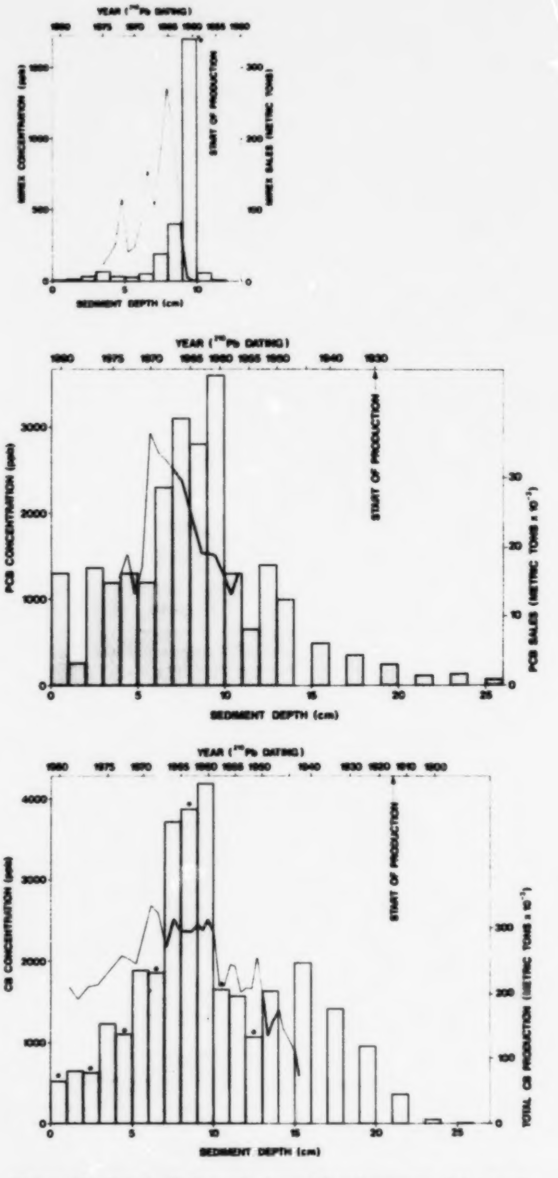

Figure 58. Total di-through hexachlorobenzenes (a); total PCBs (b); and mirex (c) vs. sediment depth and approximate date of deposition. (Total U.S. production for CBs and total sales for PCBs and mirex are superimposed; asterisks in CB diagram represent minimum values because these sections were freeze-dried.) (After Durham and Oliver, 1983).

Sediment cores from Lake Ontario have been analyzed to determine changes in historical inputs of organic chemicals to the lake and to find out the rate at which these chemicals are buried. Sediment cores from the Niagara Basin of Lake Ontario (Durham and Oliver, 1983) at a site close to the Niagara Bar where sedimentation rates are high had depth distributions of total chlorobenzenes which matched United States production figures for this chemical (Fig. 58). Maximum CB concentrations occurred at depths corresponding to the early 1960s. The same pattern emerges for PCBs (Fig. 58). Recent surficial bottom sediments immediately off the Niagara Bar have considerably lower concentrations of these chemicals than was the case in past years. Mirex (Fig. 58) is an excellent example of how a hydrophobic (highly insoluble) compound can be rapidly sedimented and buried at high sedimentation rate sites once point sources are removed. One company located on the Niagara River was the sole producer of mirex. The present low concentrations in surficial bottom sediments are similar to those now occasionally measured in suspended particulates collected at Niagara-on-the-Lake.

CHAPTER 7

# Conclusions

Several conclusions can be drawn from the results presented.

1. The operationally defined solution phase is the most important transport medium of toxic metals and organics in large rivers with low suspended particulate loads.

2. Organic chemicals, even the most hydrophobic, are primarily transported in the operationally defined "aqueous" phase, except where the suspended particulate load is very high and has a high content of organic material.

3. Suspended particulates are a major transport mechanism for toxic metals and organics and must always be considered in transport and fate models, especially in rivers with high suspended particulate loads and during peak flow events.

4. Because suspended particulates have high concentrations of toxic contaminants, they are an excellent medium for detection of toxic metal and organic sources and for routine assessment of trends in toxic contaminant loads.

5. Usually 30% or less of the common toxic metal load carried by suspended particulates and present in bottom sediments is potentially readily bioavailable. However, this proportion can vary significantly for different metals in different limnological settings. The major fraction of the particulate-associated toxic metal load is in the form of minerals or highly resistant organic material.

6. The toxic organic chemical load on suspended and bottom particulates is primarily present in this phase by exclusion from the water or by bioaccumulation, and thus in certain conditions nearly all of the sediment-associated toxic organic chemical load may become bioavailable.

7. Bottom sediments are major sinks for burial and eventual removal of toxic metals and organic chemicals from internal limnological recycling and biological food webs.

8. Field use of high-speed centrifuges to remove suspended particulates for analysis has been a major operational advance, as has the development of the aqueous liquid-liquid extractor. Some of the particulates removed by centrifuges are biotic and the centrifuge must thus be operated carefully to avoid crushing of biota with associated release of body fluids to the operational aqueous phase or breakup of naturally occurring aggregates. These processes could affect the chemical concentrations in the effluent and lead to erroneous calculation of particulate/aqueous partition coefficients.

# Research Needs

The data presented here show that considerable advances have been made in the understanding of the role of particulates in the transport and burial of toxic chemicals. Some research needs to fill knowledge gaps, particularly at complex aquatic compartmental interfaces, follow.

1. When suspended particulates are collected and analyzed for organic contaminants, the quantity of suspended solids should be measured along with their organic carbon content so that $K_{OC}$ values can be better estimated and aqueous phase concentrations better predicted.
2. At polluted sites, spatial and temporal variations in suspended particulate concentrations should be determined, for example, for nepheloid layers in the Great Lakes.
3. Sedimentation and resuspension rates for particulates should be measured at polluted sites.
4. Particle fluxes in polluted rivers should be measured, especially during events such as rainstorms or snowmelt.
5. Surface areas, morphology and surface characteristics of particulates require further quantification in terms of sorption processes relevant to contaminant bioavailability.
6. The colloidal fraction of the "aqueous" phase needs to be characterized better with respect to its role in contaminant transport and sedimentation.
7. Degradation rates and biological transfer rates need to be measured in both non-polluted and polluted aquatic ecosystems of different limnological characteristics, especially eutrophic versus oligotrophic lakes, to understand better the role of nutrient (trophic level)/contaminant interactions on contaminant fate and bioaccumulation.
8. Transfer rates of toxic contaminants into and out of bottom sediments need to be better quantified.
9. Diagenetic changes, such as methylation or complexation in bottom sediments, and the effects of these on toxic metal and toxic organic chemical bioavailability require quantification.
10. Laboratory tests of critical processes such as sorption, photolysis, hydrolysis, and degradation should continue, but the hypotheses derived should be tested more frequently in a variety of sites with different limnological characteristics. These field versus laboratory comparisons should be made for a range of organic chemicals to encompass those expected to be virtually insoluble, moderately soluble, and very soluble.

For many decades, applied limnologists have focused their research on the eutrophication issue, at best a two-contaminant (phosphorus and nitrogen) problem. Eutrophication was the issue of the early seventies. By the late seventies, acid rain replaced eutrophication as the number one issue, at least in North America. Acid precipitation per se is a four-contaminant (hydrogen, sulphur, nitrogen and aluminum) problem. Toxic chemicals are now rapidly becoming the number one global environmental issue of the eighties. The solution of the toxic chemicals problem is more complex than these former issues. Theories and hypotheses need to be formulated and tested to resolve the fate in aquatic ecosystems of thousands of existing and new toxic organic chemical compounds, as well as the several toxic organo-metallics, and the many toxic metals and radionuclides. These hypotheses must also involve an expanded understanding of the fundamental limnological processes controlling transport and fate of particulates in aquatic ecosystems.

# Part II

# Bioavailability, Recycling and Bioaccumulation

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# Abstract

Many of the more toxic organometallics and organic chemicals are strongly partitioned into and onto suspended particulates of abiotic and biotic composition and may be rapidly removed from, and buried in, aquatic ecosystems. Nevertheless, even the most hydrophobic organic chemicals such as DDT, PCBs, mirex and Kepone continue to be found at the highest aquatic trophic levels. A more recent example is the extremely toxic dioxin 2,3,7,8-TCDD. Initially, aquatic ecosystems recover rapidly once major point sources of contaminants are removed, but declines in contaminant concentrations in biota then become slower and over the short term, several years, may almost appear to have levelled off. Part of the reason is internal recycling and continued bioavailability of persistent chemicals associated with particulate matter. Physical and biological disturbance of contaminated bottom sediments is a critical process in rivers and lakes. In rivers, and even in large lakes such as the Great Lakes, physical resuspension re-introduces contaminated particulates into the water column. Biological disturbance (bioturbation) results in (1) direct biological uptake of chemicals by benthic organisms; (2) direct release of chemicals to the overlying water; and (3) reworking of surficial sediments such that the time required to bury contaminants is prolonged. The two main direct methods of assessing bioavailability of particulate-associated contaminants are described: chemical extraction and biological uptake or bioassays.

The processes above are involved in the recovery of two polluted aquatic ecosystems in Canada: (1) the English-Wabigoon River system for organometallics and (2) the Niagara River-Lake Ontario system for organic chemicals. The multi- and interdisciplinary studies conducted at these sites are reviewed to make key points concerning the process of recovery of polluted ecosystems in general. Accumulation of highly particulate partitioned toxic chemicals by organisms such as predator fish and fish-eating birds at the top of aquatic food webs is evidence of bioavailability of particulate-associated contaminants. The Niagara River-Lake Ontario ecosystem is the example used to discuss this relationship.

# Résumé

Parmi les produits chimiques organiques et organométalliques les plus toxiques, plusieurs sont fortement répartis dans et sur des particules en suspension de composition biotique et abiotique et peuvent être rapidement éliminés des écosystèmes aquatiques, ou enfouis dans ces écosystèmes. On continue néanmoins à trouver, aux niveaux trophiques les plus élevés, des produits chimiques organiques parmi les plus hydrophobes comme le DDT, les BPC, le mirex et le Kepone. Un exemple plus récent est la dioxine TCDD-2,3,7,8 extrêmement toxique. Initialement, les écosystèmes aquatiques retrouvent rapidement leur équilibre lorsque les principales sources locales de contaminants ont été supprimées, mais la diminution des concentrations de contaminants dans la biote devient alors plus lente et peut parfois sembler se stabiliser à court terme, sur plusieurs années. La raison est en partie liée au recyclage interne et à la biodisponibilité continue de produits chimiques persistants associés à des particules. La perturbation physique et biologique des sédiments de fond contaminés est un processus critique dans les rivières et les lacs. Dans les rivières, et même dans les lacs de grande superficie, comme les Grands lacs, la resuspension physique réintroduit des particules contaminées dans la colonne d'eau. La perturbation biologique (bioturbation) entraîne : 1) une absorption biologique directe des produits chimiques par les organismes benthiques; 2) une libération directe de produits chimiques dans les eaux surjacentes; 3) la remise en mouvement des sédiments superficiels, qui prolonge le temps nécessaire pour enfouir les contaminants. Les deux principales méthodes directes d'évaluation de la biodisponibilité des contaminants associés à des particules sont décrites ici; il s'agit de l'extraction chimique et de l'absorption biologique ou bio-essais.

Les processus susmentionnés interviennent dans l'assainissement de deux écosystèmes aquatiques pollués au Canada : 1) le réseau des rivières English-Wabigoon pour les substances organométalliques et 2) le réseau rivière Niagara-lac Ontario pour les produits chimiques organiques. Les études multidisciplinaires effectuées sur ces deux sites sont analysées ici afin de dégager les points essentiels concernant l'assainissement des écosystèmes pollués en général. L'accumulation de produits chimiques toxiques fortement répartis sur des particules par des organismes tels que les poissons prédateurs et les oiseaux qui se nourrissent de poissons au sommet de la chaîne alimentaire aquatique est une preuve de la biodisponibilité des contaminants associés à des particules. Cette relation est appliquée à l'écosystème du réseau rivière Niagara-lac Ontario.

CHAPTER 1

# Introduction

There is no environmental issue if (1) a toxic chemical is not measured in the environment, assuming a method with appropriate detection limits is available, and (2) there is no exposure to organisms. Another way of describing the same problem is to focus on the chemical. If a chemical is not persistent, then it can be degraded to innocuous products by biological and/or photochemical processes. However, if a compound is persistent, then it may be bioconcentrated from water or bioaccumulated via the food chain. A toxic chemical cannot be measured in an environmental medium unless it is somewhat persistent. Even relatively non-persistent compounds may be bioaccumulated before they degrade in aquatic ecosystems and may form degradation products *in vivo*. When we examine these terms which are increasingly mixed into toxic chemical issue descriptions, we see that in the long term, the chemicals of concern are those that are bioavailable. In aquatic ecosystems chemicals or elements are present in the basic non-biotic media of water or particulates in a form which results in the passage of the chemicals into and up the food chain, even to humans. In summary, higher organisms, including man, cannot be harmfully exposed to a chemical unless the chemical is persistent and unless it bioconcentrates or bioaccumulates, namely is bioavailable. Bioavailability is thus the central factor in the toxic chemicals issue.

Very persistent organic chemicals are often extremely hydrophobic and adsorb strongly to particulates. Persistent particulate-adsorbed chemicals, especially when sedimented in large lakes, are often erroneously considered to have been removed by burial from the biological food web. However, for many chemicals, such as mirex in Lake Ontario, such an hypothesis is only grossly correct because the mirex, which is almost exclusively present in the bottom sediments, is still bioavailable and is still being bioaccumulated by lake biota. Both non-persistent and persistent, and both hydrophilic and extremely hydrophobic toxic organic chemicals can all be of concern because they are all bioavailable by one process or another. Bioavailability is thus a core issue in prediction of the fate of any new chemical to be released to an aquatic ecosystem. It becomes essential to know why, and for how long, various chemicals are bioavailable. The answers to these questions are partly related to the properties of the chemical but, of equal importance, to the controlling limnological processes in specific aquatic ecosystems.

By definition, the eventual presence of an element or chemical in the tissues of living organisms means that it was bioavailable. Bioavailability can be strongly influenced, but not necessarily controlled, by the form (or speciation) of an element or compound in the aquatic environment. Speciation is of critical significance for some metals because their organometallic forms or species are usually more toxic.

Most of the particulates in a river/lake system are present as bottom sediments which are moved over, through or lived in by a variety of benthic biota covering a wide range of trophic levels. Suspended and resuspended sediments in rivers and lakes are also media that are in intimate contact with a variety of aquatic biota. Suspended particulates may be both abiotic and biotic. In all forms, particulates can have organic and organometallic contaminants adsorbed on their surfaces or contained within them. The aqueous fraction of "water" is usually defined operationally as the material that passes through a 0.45-$\mu$m filter or is the fraction that is not removed by high-speed centrifugation. Both abiotic and biotic particulates do pass through 0.45-$\mu$m filters. Inorganic, very fine clay size particles ($<0.08\ \mu$m) and much of the fibrilic and colloidal material in natural waters even pass through high-speed field centrifuges. These "aqueous" phase particulates must not be overlooked in a discussion of particulate (associated chemical) bioavailability.

The role of particulates in bioavailability must acknowledge the many processes of sediment/water interaction in aquatic ecosystems. Bottom sediment contaminant bioavailability involves interactions with overlying waters by sediment resuspension, bioturbation, and pore water release. In the overlying water, there are many biotic-abiotic interactions between chemicals in true solution and present as precipitates, colloids or the larger suspended abiotic and biotic particulates that make up the suspended particulate phase. Sediment partitioning of chemicals reduces their exposure to biota from the water phase. However, the concentrations of chemicals in water are so low as to require years of ingestion to reach the same level of exposure as may be obtained by ingestion of particulates. In bottom sediments, the basic food is organic debris. Many benthic and filter-feeding organisms pass large volumes of particulates and their associated chemicals through their digestive systems. Fish also may accumulate chemicals by direct desorption from or ingestion of suspended particulate-associated contaminants. The role of direct desorption of contaminants from particulates to fish remains controversial but needs to be resolved. For hydrophobic contaminants such as PCBs, mirex or dioxin, one meal of fish can equal 20 to 25 years of human exposure to water.

Bioavailability of particulate-associated contaminants depends on physical, chemical and biological processes, including chemical adsorption, desorption; diffusion and remobilization; physical resuspension; bioturbation; and direct uptake by biota. The main factors involved are

(1) The properties of the element or chemical

(2) The properties of the particulates

(3) The chemical properties of the "aqueous" phase (pore water or overlying waters), especially pH, Eh, salinity and the concentrations of organic and inorganic complexing components.

Many of the environmental interconnections affecting the bioavailability of particulate-associated toxic organometallic and organic chemicals are shown in Figure 1. Most of the examples to be discussed later come from recent research in Canada into the pollution problems of (1) the Wabigoon-English River system of northwestern Ontario (Allan *et al.*, 1984) and (2) the Lake Ontario-Niagara River System (Allan *et al.*, 1983).

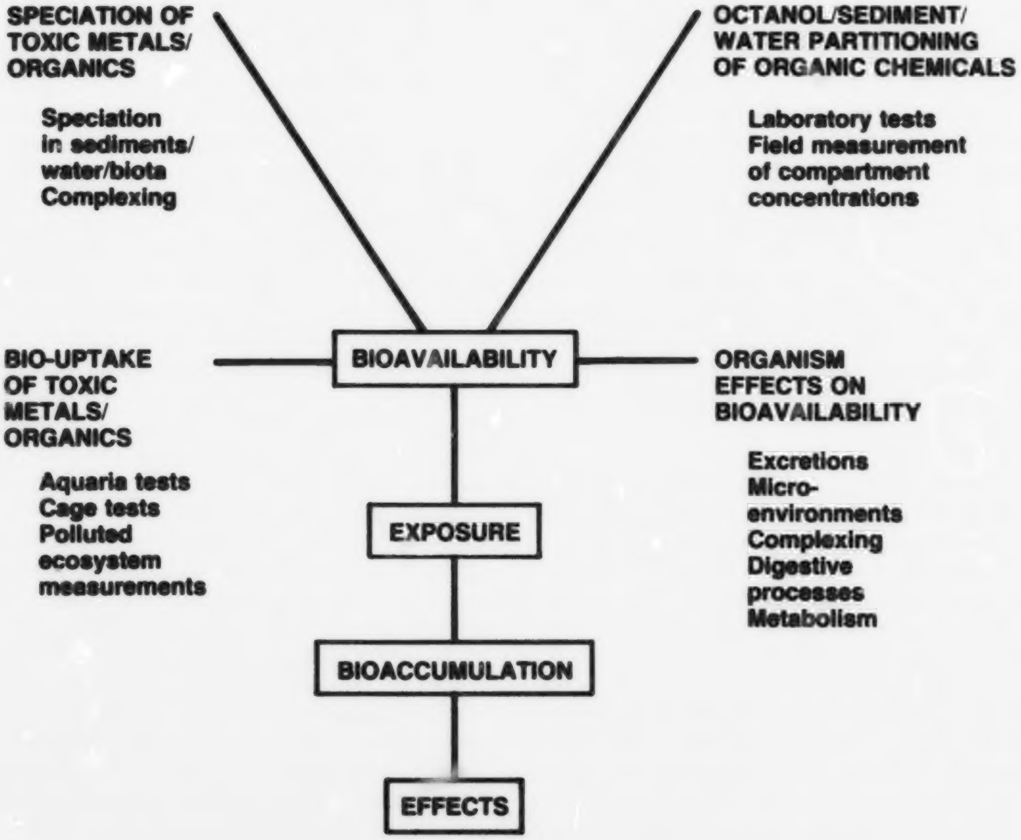
SPECIATION OF TOXIC METALS/ ORGANICS
Speciation in sediments/ water/biota
Complexing
OCTANOL/SEDIMENT/ WATER PARTITIONING OF ORGANIC CHEMICALS
Laboratory tests
Field measurement of compartment concentrations
BIO-UPTAKE OF TOXIC METALS/ ORGANICS
Aquaria tests
Cage tests
Polluted ecosystem measurements
BIOAVAILABILITY
ORGANISM EFFECTS ON BIOAVAILABILITY
Excretions
Micro-environments
Complexing
Digestive processes
Metabolism
EXPOSURE
BIOACCUMULATION
EFFECTS

**Figure 1. Research fields relevant to bioavailability of particulate-associated contaminants.**

CHAPTER 2

# Overview of Approaches to Assessing Contaminant Bioavailability and Factors Affecting Contaminant Recycling

Many toxic organic chemicals have extremely low solubilities, such that they become associated with solid phases. Sedimentation of these solids builds up high (relative to the overlying water) concentrations of toxic chemicals in bottom sediments, and there are many examples of this from coring of river and lake bottom sediments, as discussed in Part I. Perhaps then the major route by which particulate-associated organic contaminants are bioaccumulated is by direct uptake by benthic organisms which form the lowest levels in many aquatic food webs. Hence, bioavailability of chemicals in bottom sediments may be seen as one of the central questions in any long-term prediction of the fate of persistent toxic chemicals in aquatic ecosystems. The classic example is mercury which, when released in the metallic form, was known to be rapidly sorbed by particulates, sedimented, and thereby assumed to be rapidly removed from aquatic food webs. The discovery that Hg was converted to an organometallic form by bacterial processes in bottom sediments changed the convenient burial scenario forever. The same principle applies to persistent toxic organic chemicals such as mirex in Lake Ontario or Kepone in the James River. Both of these organic compounds are extremely insoluble in water and are known to be strongly sorbed to particulates. They are both found in highest concentrations in particulates and were thus expected to be effectively and efficiently removed from the food web. Both compounds, however, continue to bioaccumulate into higher organisms, some of which are eaten by humans. In the Laurentian Great Lakes, concentrations of mirex in fish are still at levels such that guidelines must be followed for fish consumption by humans. Thus, although hydrophobic organic chemicals can be rapidly buried in bottom sediments, as shown in Part I, this is often far from the end of their fate, at least in the short term of decades.

There have been two major scientific approaches to the estimation of the degree to which bottom sediments affect concentrations of toxic organic chemicals in biota (Fig. 1). The first, which dominates the literature, is based on laboratory bioassays in which various biota are exposed to polluted sediments and their uptake of various chemicals measured. The second and less documented method is to analyze the various biota that have an association with bottom sediments in polluted ecosystems and to see whether there is a relationship between chemicals found in the sediments and in the benthic biota. Bioaccumulation of particulate-associated chemicals from bottom sediments begins with uptake by benthic organisms, followed by trophic transfer up the food chain. The physical movements or migration of biota may transfer contaminants vertically and horizontally to different locations. Transfer may involve intermittent movement by biota in and out of bottom sediments and even as far as to the surface of deep lakes. Movement may be regular or diurnal. Contaminants may be re-deposited by biodeposition at new locations or by release of gametes or young. Many benthic biota mix contaminants into sediments by bioturbation. Certain fish burrow into and stir up polluted surficial sediments. The bioavailability of contaminants in bottom sediment pore waters is an important factor controlling benthic bioaccumulation of contaminants. However, pore waters are seldom collected and analyzed for toxic organic chemicals. A greater understanding of the partitioning of contaminants between bottom sediments and pore waters is an important knowledge gap in contaminant fate research. Some biota have the ability to absorb contaminants directly from sediments through their body walls or exoskeletons. Deposit feeders are likely to concentrate those chemicals which occur predominantly in pore waters, whereas filter feeders may concentrate chemicals that are more strongly partitioned onto the sediment phase. Rooted water plants are likely to absorb chemicals primarily from the water. On senescence of these plants, benthic detrital feeders may accumulate the toxic chemicals from the decaying plant tissues. Benthic invertebrates are the principal consumers of contaminated plant detritus. Sublethal contaminant levels may cause a deterioration of avoidance by prey, which in turn may have a lethal effect on the predator species. Once in the food web, effects of trophic transfer are important for biomagnification of toxic contaminants.

Most sediment bioavailability research in Europe has taken place in Germany and has been a response to the need to assess the bioavailable toxic metal contents of riverine dredge spoils destined for disposal in marine settings. Most research has been with heavy metals. The methods have relied heavily on the development of sequential chemical extraction techniques (Förstner and Wittmann, 1981; Förstner, 1982; Salomons and Förstner, 1984). These techniques were reviewed in Part I because they are equally relevant to resolving the transport phases of toxic metals. More recently, bioassays have used sediment elutriates. Other common techniques to assess bio-uptake use microcosms, limnocorrals or caged biota. All are attempts at direct measurements of the bioavailable contaminant content of sediments. An indirect method of assessing bioavailability of sediment-associated contaminants is the study of contaminated ecosystems.

Even the direct chemical release, recycling or "bioavailability" of metals from bottom sediments in acid-stressed lakes is still not absolutely established. Results for a lake in southern Norway (Ruether *et al.*, 1981) show that levels of Zn and Cd decline in the upper layers of the lake bottom sediments. Zinc has been removed from the easily extractable fractions, while Cd has been removed from the organic fractions (Fig. 2). The lake had a pH of 4.4. The same release did not seem to occur in a nearby lake with pH 4.9. These sediment fractions are those in which Zn and Cd are primarily present in suspended particulates during transport. The direct chemical release of organic chemical contaminants from sediments is even less established. Laboratory experiments in which overlying water is continually replaced over PCB-contaminated sediment show that the chemical slowly re-establishes equilibrium. Results for PCB distribution in the Hudson River and for methyl-Hg in the Wabigoon River "imply" a steady return of chemicals from bottom sediments to the overlying water.

Complexing of toxic metals may or may not reduce their toxicity to biota. Free Cu and Zn ions are more toxic to biota than their organically complexed forms. The role of cytoplasm is important in resolving forms of passage of metals across cell walls and the ability of cells to release metals or metal complexes back through the cell walls. Complexation enhances uptake and toxicity of other metals, as has been shown for Hg, Pb and Cd. Sediments may thus detoxify metals by decreasing the dissolved metal concentrations. Förstner and Salomons (1983b) have reviewed interactions between metals and organisms. The major routes of metals uptake are displayed in Figure 3. Producers accumulate from the exchangeable or complexed pool of toxic metals. Consumers are able to accumulate from the more firmly bound phases. These principles for toxic metals are partly applicable to particulate-associated toxic organics. Partitioning or speciation studies of toxic metals in bottom sediments show that at different locations, different metals are associated with different phases. If there are general rules, then Cd usually is associated with the organic phase and Zn with the carbonate phase. The metals Pb, Zn, Cd, Cu, Ni and Cr are often associated with the organic matter in bottom sediments. Methylmercury is far more toxic than elemental Hg but comprises only a small fraction of the total Hg present in aquatic ecosystems. Lead is more toxic when present as methyl-Pb, and there is some indication that methylation of Pb takes place in aquatic environments. More likely, tri-alkyl lead is formed by degradation of tetra-ethyl lead. Tin is also present in aquatic environments in the more toxic alkylated forms and is bio-accumulated. Generally, for Hg, Pb, Sn and As, organic complexation increases lipophilicity, bioavailability and toxicity of the element. Most of the aquatic methylation processes occur in bottom sediment by bacterial reactions. Thus, benthic detritus feeders and benthic organism predators are important in the initial transfer of organometals into the food web. The interactions between bacterial degradation and incorporation of organometals into food webs require further elucidation.

Heavy metal bioavailability can be estimated by benthic organism uptake (Luoma and Bryan, 1979) and the same technique has been used for toxic organic uptake from sediments as discussed below. However, even for toxic metals, experiments on bio-uptake from contaminated sediments are seldom correlated with analyses for metal species in the sediment. Also, these techniques try to estimate the bioavailable contaminant content but make little attempt to measure the effect of the bioavailable contaminant fraction in the same sediments. With organic chemicals, the situation may be simpler because all of the anthropogenic toxic organic chemical content may be considered to be potentially bioavailable. However, an area of research which seems to be disregarded is the development of sequential extraction procedures for toxic organics. Such a procedure might separate the sediment-bound, toxic organic component into easily and moderately bioavailable fractions. Determination of such fractions may then be combined with bioaccumulation results. Sediments used for partitioning experiments should at least be studied simultaneously for direct bio-uptake.

Dredging and open water disposal of sediments disperse pore fluids and mineralized organic matter into new chemical surroundings. Physical resuspension of lake and river bottom sediments invariably does the same. The impact of dredging reveals much about the impact of bottom sediment resuspension and the impact of the bioavailable toxic component of bottom sediments. Many of the major rivers and harbours of the world already contain severely contaminated sediments. Dredging of these sediments is often required, and open-water disposal is common and has led to the development of a small cadre of experts working on the improvement of methods for measuring the

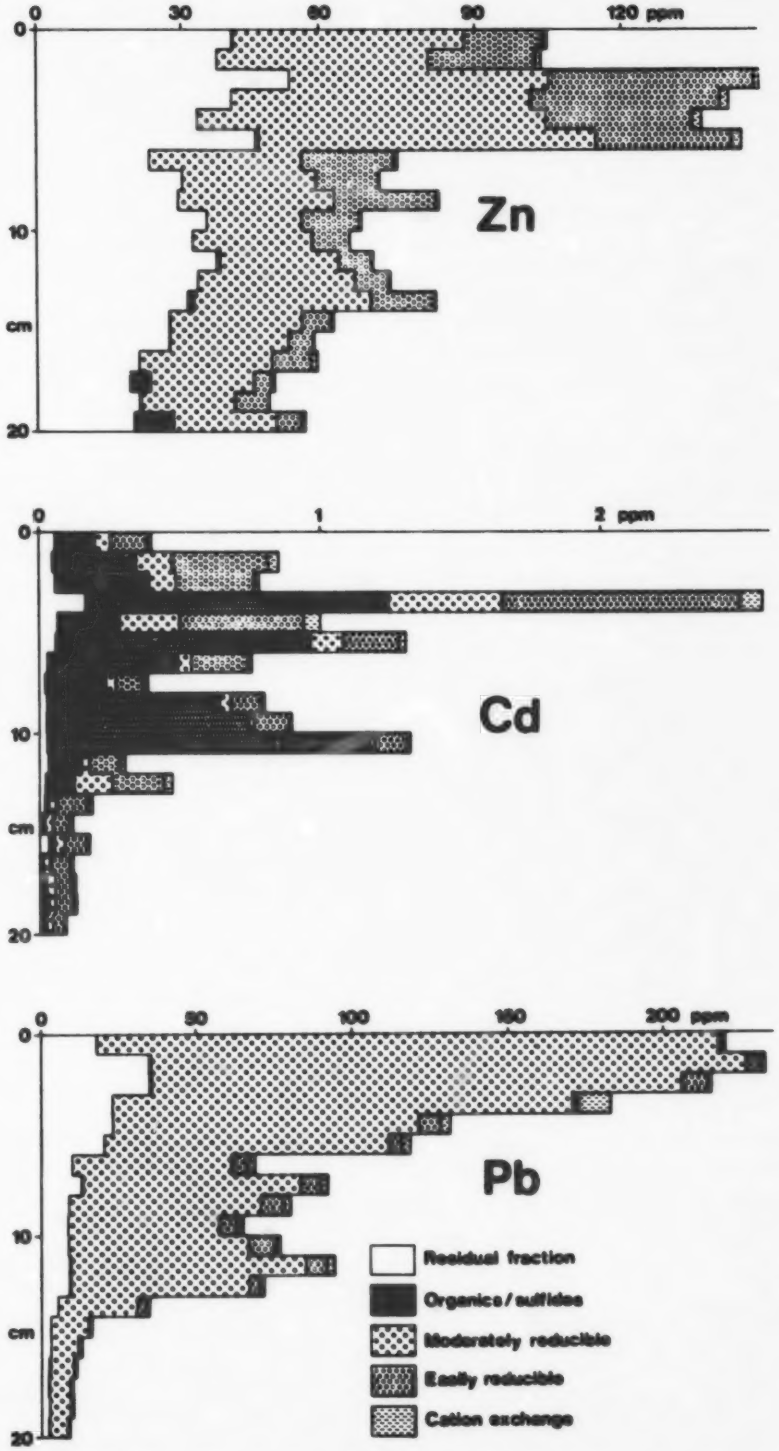

**Figure 2.** Depth profiles of zinc, cadmium and lead chemical forms in a sediment core from Lake Hovvatn, Norway (after Ruether *et al.*, 1981).

bioavailable component of dredged sediments and its effect on aquatic biota. Munawar *et al.* (1983) reviewed methods of assessing biological effects of dredge spoil contamination and developed a fast and sensitive bioassay to measure these effects. The sediment-water mixture is agitated for 30 min with air and after one hour of settling is filtered through a 0.45-$\mu$m filter. Half of the elutriate is passed through a Chelex-100 resin to remove dissolved metals. Both the original elutriate and that with dissolved metals removed are used in bioassays using different elutriate concentrations. The standard elutriation uses one volume of fresh sediment and four volumes of the disposal site water. Natural phytoplankton from the disposal area are used as the test organisms and species counts are made. Research into bioaccumulation of sediment-bound organics by phytoplankton apparently has not been studied, although uptake of nutrients and toxic metals directly from sediments by algae has been examined by a few researchers.

Examples of the chemical and physical effects of organisms on metal bioavailability have been summarized by Salomons and Förstner (1984):

(a) Change in environmental conditions due to pH increase, e.g., algal blooms in lakes

(b) Reduction of sulphate to sulphide in sediments by bacteria and subsequent formation of metal-sulphide compounds

(c) Redox conversions of inorganic forms, e.g., the oxidation of manganese, iron and arsenic

(d) Conversion from inorganic to organic forms, and vice versa, typically methylation and demethylation

(e) Production of pseudofeces by bivalves in tidal areas, changing the settling properties of the suspended matter and enhancing sedimentation

(f) Bioturbation of upper sediment layers

(g) Release of extracellular material by algae (fibrils).

Microorganisms are known to produce large quantities of extracellular polysaccharides, which are organized in well-defined capsules around the cells or are secreted as loose material. By complexing metals and reducing the activities of metal ions, extracellular algal products can change the

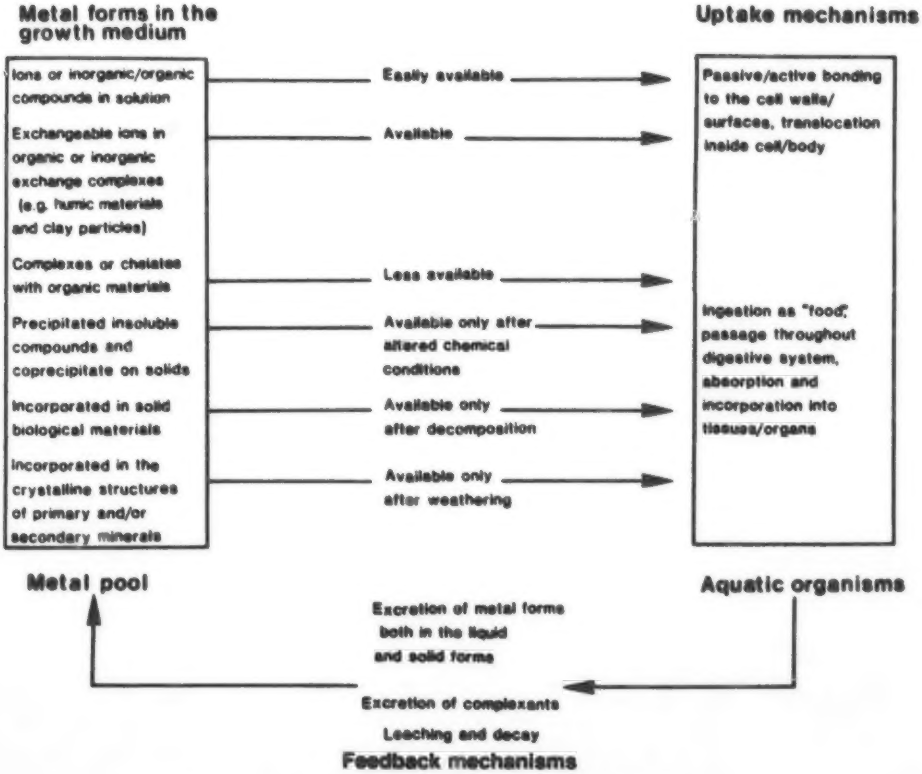
Metal forms in the growth medium
Uptake mechanisms
Ions or inorganic/organic compounds in solution
Easily available
Passive/active bonding to the cell walls/surfaces, translocation inside cell/body
Exchangeable ions in organic or inorganic exchange complexes (e.g. humic materials and clay particles)
Available
Complexes or chelates with organic materials
Less available
Precipitated insoluble compounds and coprecipitate on solids
Available only after altered chemical conditions
Ingestion as "food", passage throughout digestive system, absorption and incorporation into tissues/organs
Incorporated in solid biological materials
Available only after decomposition
Incorporated in the crystalline structures of primary and/or secondary minerals
Available only after weathering
Metal pool
Aquatic organisms
Excretion of metal forms both in the liquid and solid forms
Excretion of complexants
Leaching and decay
Feedback mechanisms

Figure 3. Bioavailability of metal forms (after Baudo, 1982).

speciation of metals and possibly detoxify the external milieu of a cell. Complexation by extracellular algal products can dominate the speciation of copper in natural waters and lower the toxicity of copper. However, a detoxifying role can be envisaged only when the organic copper complexing compounds are not rapidly degraded. Most of these organism effects could be equally important in terms of the bioavailability of toxic organic chemicals. Another important but little researched aspect of toxic metal and organic chemical bioavailability is that organisms may not be passive accumulators. There may be specific mechanisms by which certain organisms mobilize specific sediment-bound fractions with a greater degree of uptake of metal and organic contaminants than might be expected. Such processes are well known from research into plant root/soil interactions.

Sediments are an ultimate sink for contaminants, once the depth of burial is beneath the zone of bioturbation and possible physical erosion and resuspension. However, near the surface of bottom sediments, two-directional exchanges do occur, depending on the character of the sediment and of the overlying water. The equilibrium is dynamic in the sense that the factors affecting exchange one way or the other can change rapidly in natural systems. Cleaner overlying water can result in greater release of bottom sediment-bound contaminants. Several factors affect the exchange of chemicals from bottom sediments to water, including

(1) *Physical factors*

Temperature, hydrodynamics and mixing.

(2) *Biological factors*

Bioturbation, organism ecology and physiology.

(3) *Chemical factors*

Acid-base reactions, complexation, oxidation-reduction, adsorption-desorption, precipitation-dissolution.

Temperature can affect reaction rates, including degradation rates. Physical mixing can occur even in deep stratified lakes. In rivers, physical resuspension and mobilization of contaminated sediment, especially in high-flow periods, make contaminated rivers a long-term source of contaminants to downstream sites. Biota directly or indirectly mix surface sediments sometimes by producing gases which cause this mixing. Reduction of toxic metals to insoluble metal sulphides is important. In eutrophic systems, changes in hypolimnion chemistry related to biological activity may effect metal speciation. Most reactions are thus very ecosystem-specific. Changes in pH can affect sorption sites; the occurrence of precipitation and complexation reactions; and the nature of ionic species themselves. Complexation reactions in the water phase can cause greater release of metals from sediments. Fulvic and humic acids and fibrilic materials are all capable of complexing toxic metals. All of these are, of course, ecosystem-specific. As the redox-potential of sediment drops there is increased mobility of bottom sediment-associated toxic metals. Sediments at depth are reducing, but depending on the trophic state, the sediments at the surface and the overlying water can be either reducing or oxidizing. Redox is important in mobilizing iron which, in turn, affects the bioavailability of several toxic metals. There are both mineral and organic sorption rates in sediments. Sorption is pH-dependent and somewhat reversible. Precipitation and dissolution are important for metals such as Zn which often occur in bottom sediments as carbonates. All these factors and processes can effect a release of toxic metals and organic chemicals sorbed to or occluded in sediments.

## CHAPTER 3

# Biological Estimates of Contaminant Bioavailability

The test organisms most commonly used to assess bioavailability of contaminants in sediments are various types of worms. Sediments are either spiked with contaminants, sometimes radiotracers, or are sediments from polluted aquatic ecosystems. In the United States, organisms such as prawns or clams are usually exposed to dredged sediments containing high chemical concentrations. Some organisms seem better suited for tests with toxic metals; others for toxic organics. The uptake of particulate-associated contaminants has been described for a variety of freshwater biota. As an example of the extreme complexity of the problem, Förstner and Salomons (1983a) asked "How much of a metal is taken up by diffusion through the foot of a mussel?" and such information may, in fact, be important.

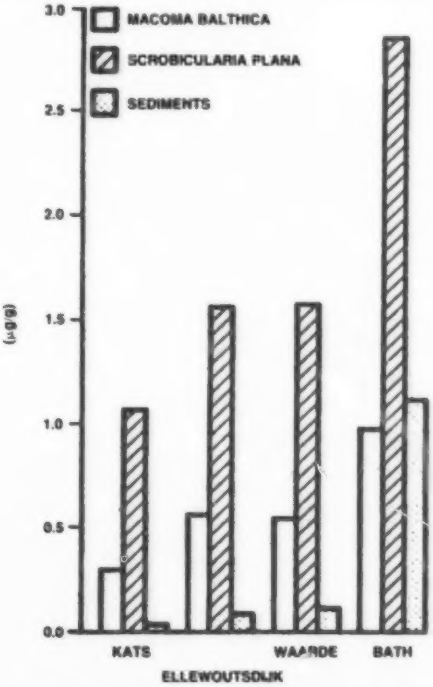

**Figure 4.** Metal concentrations in *Macoma balthica* exposed to the same concentrations of metals in surface waters (Eastern Scheldt, The Netherlands) but to different sediment concentrations (after Salomons and Förstner, 1984).

The concentrations of metals in benthic biota generally reflect the concentrations in the sediments with which they are associated in test ecosystems (Fig. 4). The same applies to sediment-bound organic chemicals. However, there is no simple, specific relationship between total toxic contaminant concentrations in bottom sediments and uptake by organisms. Luoma and Jenne (1976) found that *Macoma balthica* uptake of Cd and Co correlated with the 70% ethanol or 1 $N$ $NH_4A\bar{c}$ extracts of San Francisco Bay sediments and that the Cd, Co and Zn uptake correlated with weak acid (0.1 $N$ HCl; 2% acetic acid) extracts. Extractions with reducing agents such as 1 $N$ $NH_2OH$ HCl in 0.01 $N$ $HNO_3$, sodium-citrate bicarbonate dithionite (Na-CBD), or oxidizing agents such as $H_2O_2$ produced poor correlations with bioaccumulation. The same variations in degree of uptake of different chemicals from different sediments by different biota occur with toxic organic compounds. Hence, even for toxic metals, the present state of correlation between bioaccumulation of metals from sediments to organisms and sediment metal speciation is far from satisfactorily resolved, and considerably more studies have been made with toxic metals than with toxic organic chemicals. However, for toxic metals in general, a weak acid-reducing extractant seems to offer the best indication of the metal bioavailable fraction for practical purposes. The best chemical extractant for the best estimate of the bioavailable particulate-associated toxic organic content remains to be determined.

Benthic organisms affect the bioavailability of particulate-bound contaminants in bottom sediment by

(a) Redistributing the contaminants in the surface sediment layers (bioturbation)

(b) Causing their release by physical disturbance

(c) Biodegrading the contaminants

(d) Accumulating them by direct sorption (bioconcentration) and biomagnification.

Most physical disruption and mixing of contaminants in surficial bottom sediments is thought to be related to oligochaete abundances. This is why laboratory studies of uptake of sediment-associated contaminants make prime use of these and various other worms found in freshwater and marine environments. A second organism which now is also thought to play an important role is the amphipod. A third, which has even more profound implications because of its daily migration from sediment surface to relatively shallow depths, is the freshwater shrimp (Mysids).

Tatem (1982) used freshwater prawns and clams to determine bioaccumulation of PCBs from dredge spoil. Clam tissue contained 23.8 ppm PCBs versus the contaminated sediment concentration of 9 ppm, or the bioconcentration factor was 2.43. Oligochaetes digest sediments, breathing through their posterior end. They expel feces at the bottom sediment surface. Appelby and Brinkhurst (1970) determined the effect of temperature on the defecation rate of tubificid oligochaetes and found that rates were greater at higher temperatures. McLeese *et al*. (1980) measured the uptake of PCBs from sediments by worms and shrimp and found that the accumulation of PCBs from sandy sediment by the worms (*Nereis virens*) was related to concentration in the sediment and time and inversely related to worm size. The PCBs were not excreted and no equilibrium concentration was attained. Bioconcentration factors were from 3.8 to 10.8. The same correlations were found with the shrimp (*Crangon septens spinosa*). Bioconcentration factors were 1.9 to 3.5. Bioaccumulation by smaller organisms results in higher concentrations of PCBs (Fig. 5). The same effect was seen with the shrimp as with the worms. The uptake of PCBs by clams occurred rapidly for the first 20 days and then appeared to level off (Fig. 6). Although the data have considerable scatter, the same general relationship was also found for prawns but with a greater scatter of the data points. Rubinstein *et al*. (1980) examined the uptake by oysters of Kepone from contaminated sediments and found a correlation between the sediment Kepone concentration and the residues in oysters and lugworms at the end of a 28-day exposure period (Fig. 7).

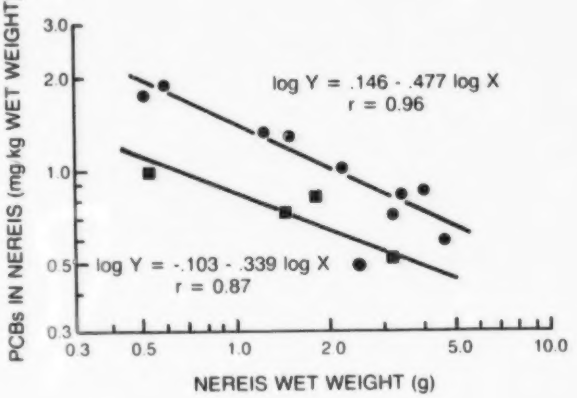

Figure 5. Aroclor 1254 concentrations in *Nereis virens* (.05 to 4.7 g) exposed for 32 days to sandy sediment with 0.17 μg PCBs/g sediment (dry weight) (after McLeese *et al*., 1980).

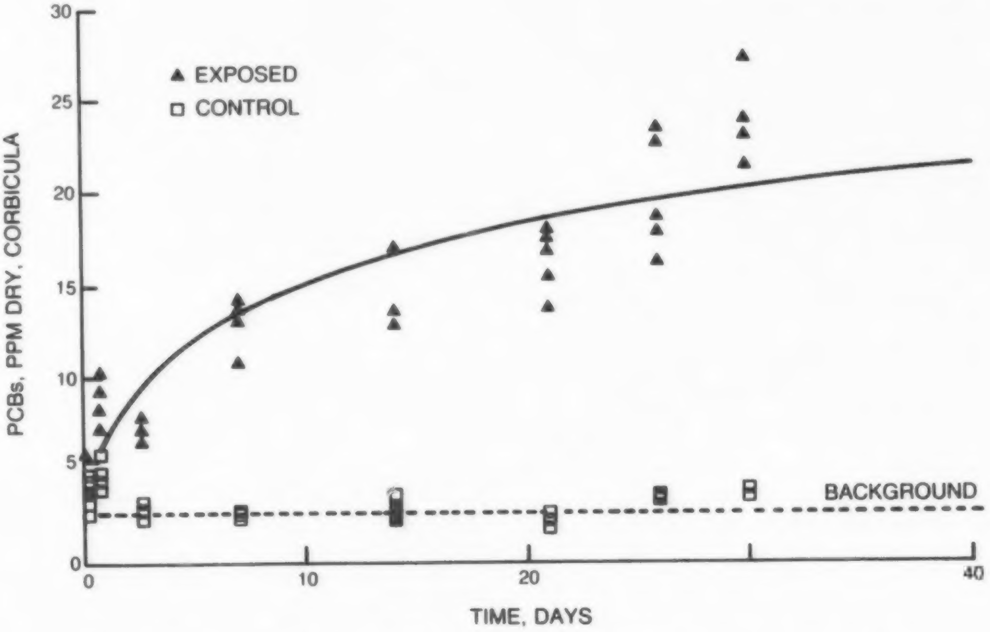

Figure 6. PCB content of clams exposed to sediment containing 9.8 ppm PCBs (after Tatem, 1982).

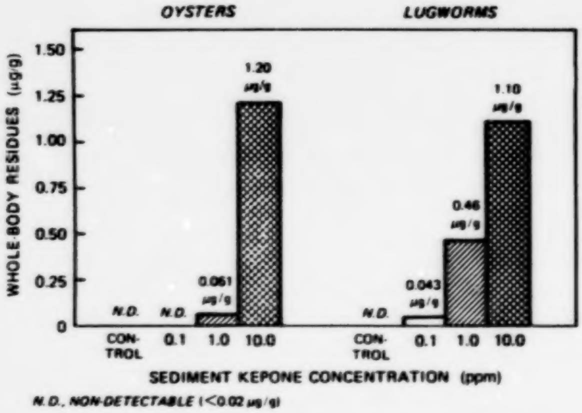

**Figure 7.** Kepone residues in oysters and lugworm following a 28-day exposure to Kepone-sorbed sediments (after Rubinstein *et al.*, 1980).

Thus *organism size* and *time of exposure* affect the final concentrations in biota. A third factor is obviously the *concentration of the contaminant in the sediment* as demonstrated by Fowler *et al.* (1978) for PCB uptake by the worms (*Nereis diversicolor*) (Fig. 8). A period of 20 days or less accounts for most of the bioaccumulation, at least at lower PCB concentrations. The equilibrium concentration factors were 3 to 4 after two months. Polychlorinated biphenyl elimination rates followed the same pattern, with higher loss rates in the worms with the higher concentrations. Accumulation of PCBs from water was faster with bioconcentration factors of up to 800, but uptake from the sediments was important in terms of absolute concentration in the worms. Elder *et al.* (1979) found that worms bioconcentrated PCBs by a factor of 3.5 and noted that PCBs accumulated in bottom sediments are depurated to the overlying water and can then be taken up directly by bottom-dwelling fish. Goerke *et al.* (1979) found that the marine sandworm (*Nereis virens*) given PCB-contaminated food accumulated the PCBs, depending on the number of chlorine atoms and on their position in the PCB molecule. In other words, *chemical structure* was a fourth factor affecting uptake of organic chemicals. They found that the PCBs with more chlorines were bioconcentrated to a greater extent (di-0.9; tri-1.3; penta-2.5). The lesser chlorinated PCBs were also eliminated faster. Langston (1978) determined PCB uptake by marine bi-values (*Cerastoderma edule* and *Macoma balthica*). Selective accumulation of PCBs with five chlorine atoms (Fig. 9) again demonstrated the importance of structure in bioavailability of organic chemicals. Isomers of low and very high molecular weight were accumulated at much slower rates. The primary route of uptake of sediment-bound PCBs by the bi-valves was by filtration and ingestion of particles.

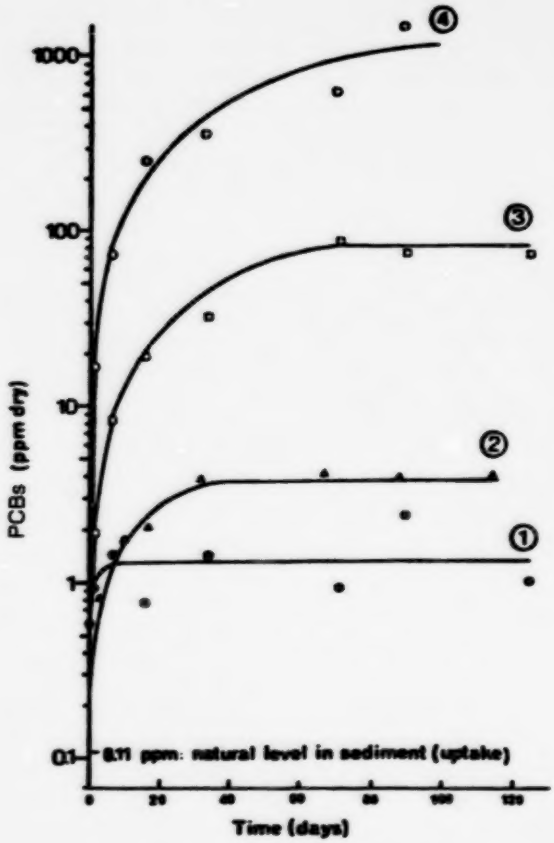

**Figure 8.** *Nereis diversicolor* accumulation of PCBs from sediments spiked with 0.65 ppm (Curve 2, triangles), 9.3 ppm (Curve 3, squares), and 80 ppm (Curve 4, open circles) dry weight. Curve 1 (solid circles) represents PCB levels in worms living in unspiked sediments. Wet weight to dry weight ratios are 5.6 for worms and 2.2 for sediments (after Fowler *et al.*, 1978).

The *character of the sediment* is a major factor affecting bioaccumulation of bioavailable contaminants in sediments. Lynch and Johnson (1982) demonstrated that the sediment organic matter content and particle size, two parameters themselves often closely correlated, affected the bioaccumulation of hexachlorobiphenyl (HCBP) by amphipods. When the sediment organic content was removed, the amphipods accumulated more HCBP. Sediment organic content thus reduced bioavailability of sediment-associated organic chemicals. Particle size was less important in this aspect than sediment organic content.

Contaminated sediments from Lake Ontario have recently been used by Oliver (1984) to investigate the role

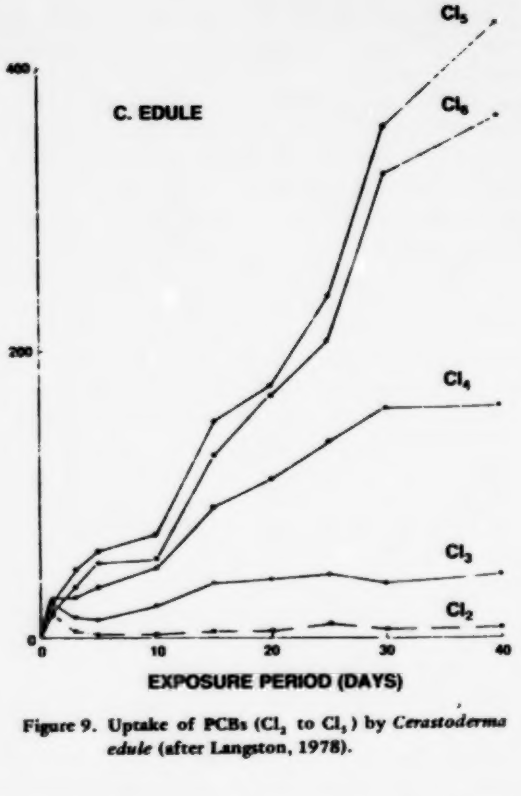

**Figure 9.** Uptake of PCBs ($Cl_2$ to $Cl_5$) by *Cerastoderma edule* (after Langston, 1978).

of oligochaete worms (*Tubifex tubifex* and *Limnodrilus hoffmeisteri*) in bioavailability of sediment-associated organic contaminants. The experiments were carried out in aquaria. The results for these freshwater worms were in general agreement with reported results with marine worms; namely, higher initial sediment concentrations, longer times of exposure, and smaller worm size, all resulted in greater bioconcentration factors. Different chemicals and isomers were bioconcentrated to different degrees so that the worms ended up with different chemical and isomer mixtures than were in the original contaminated sediments; hence worm predators would be exposed to different chemical mixtures than are present in the bottom sediments per se. The bioconcentration factors for specific chlorinated benzenes were much higher in actual worms taken from Lake Ontario and analyzed than those which bioaccumulated their isomers in the laboratory tests. For example, BCFs for pentachlorobenzene and hexachlorobenzene were 0.3 and 0.5 in the laboratory and 1.3 and 1.9 in the lake. One possible explanation is the effect of different pressure and temperatures between the field and laboratory settings, namely 8 atmospheres and 4°C versus 1 atmosphere and 20°C, respectively. The lake worms, however, were generally smaller. It may be necessary to construct special pressure and temperature tanks in laboratories to simulate true field conditions. In laboratory tanks, worm fecal pellets were found to contain the same concentration levels of contaminants as the contaminated sediments. In the most contaminated sediments, PCB biota/sediment bioconcentration factors were in the same order (1.4 to 5.1) as found with the marine polychaete (*Nereis diversicolor*) (Elder *et al.*, 1979). A wide range of bioconcentration factors (0.06 to 6.7) was observed for the various chemicals over the 110-day tests (Oliver, 1984). These bioconcentration factors were plotted against octanol/water partition coefficients ($K_{OW}$) for the chemicals. A slow linear increase in bioconcentration factor (BF) with $K_{OW}$ was observed for chemicals with $K_{OW}$'s less than $10^5$; a rapid increase in BF occurs for chemicals with $K_{OW}$'s between $10^5$ and $10^6$ followed by a drop in BF for chemicals with very high partition coefficients $>10^5$ (Fig. 10). One possible explanation for this is that the chemical uptake and elimination rates by the worms may have reached equilibrium during the study and that BFs are mainly governed by compound lipophilicity, i.e., $K_{OW}$. Most compounds with $K_{OW}$'s between $10^5$ and $10^6$ are likely to have long half-lives in fish and other biota, and so equilibrium concentrations may be difficult to achieve (Oliver and Niimi, 1983). If the worms are unable to eliminate the chemical (or eliminate it too slowly), the chemical concentrations in the worm may build up over time. The BFs for all chemicals with $K_{OW}$'s between $10^5$ and $10^6$ steadily increased over the study period. The observed decrease in BFs for chemicals with very high $K_{OW}$'s $>10^6$ could occur because these chemicals may be more strongly bound to the sediments, making them less bioavailable, or because of difficulty in chemical transport across worm membranes due to large molecular size.

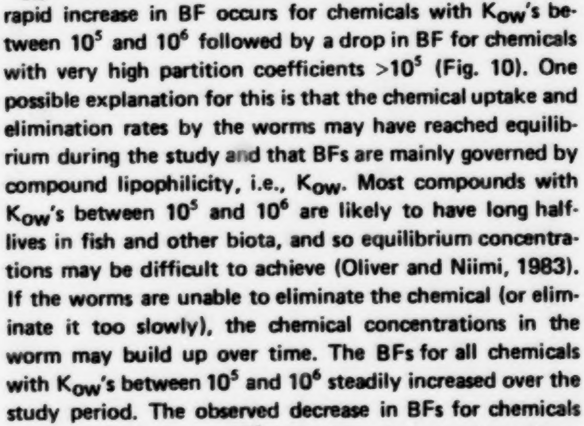

**Figure 10.** Bioconcentration in oligochaete worms vs. chemical octanol-water partition coefficient ($K_{OW}$) (after Oliver, 1984).

The common PAHs present in Lake Ontario sediment are perylene, benzopyrenes and benzofluorantenes (Strosher and Hodgson, 1976). Maximum concentrations were found in the surface 5 cm of Lake Ontario sediment, with total concentration of aromatics around 3 $\mu$g/g versus approximately 0.1 $\mu$g/g below 25-cm depth. Few PAHs are detectable in Lake Ontario water and those that are, such as methyl naphthalenes, occur at concentrations of 3 to 500 ng/L, or some $10^3$ to $10^6$ times less than in the surficial bottom sediments. To determine biomagnification, Eadie *et al.* (1983) analyzed amphipods, chironomids and oligochaetes and associated contaminated sediments in the Great Lakes for PAHs. The concentration of some PAHs in *Pontoporeia hoyi* was increased by some ten times over concentrations in the bottom sediments with which they were in contact (Fig. 11). For other PAHs, *Pontoporeia hoyi* was in approximate equilibrium with sediment concentrations. Similar equilibria were found with oligochaetes and chironomids (Fig. 12). However, chironomids biotransform PAHs so that apparently lower eventual bioaccumulation occurs. Mixing of the top few centimetres of sediment by oligochaetes prolongs exposure of benthic organisms such as *Pontoporeia* which plough through the very top layers of bottom sediments. In the Great Lakes, amphipods are a major dietary component for all fishes at some stage in their life and are a major route of exposure. The same applies to a variety of other toxic organic chemicals. Pore water concentration distributions of PAHs were similar to those in the sediments only on a gross scale. Very fine particulates may be included in pore water extracts. The PAHs in *Pontoporeia* correlated best with PAHs in the finer sediment fractions which serve as food sources. Correlations need to be made between field sediment and benthic organism organic concentrations and site-specific, bottom sediment particle size ranges. Sediment-associated PAHs are responsible for a large portion of the body burden of PAHs in some biota, and this is related to both the grain size of the sediments and the solubility of the individual PAHs. Although several benthic organisms accumulate PAHs to relatively high levels, bioaccumulation to higher trophic levels does not seem to occur, at least for bottom-feeding carp and the predatory Coho salmon in Hamilton Harbour, Lake Ontario (Hallett and Brecher, 1984). The respective levels for benzo (a) pyrene of 138 ppt and 69 ppt in fresh fillets may be related to the degree of biomagnification found in lower organisms which derived their PAH body burdens by direct association with PAH-contaminated bottom sediments. However, PAHs may be biotransformed by fish. There is interest in PAHs because contaminated sediments have been shown to produce cancer in fish (Black, 1983). Contaminated sediments can apparently generate skin tumours in fish by surface contact alone. Such cancerous or ecosystem health effects on fish of sediment-bound contaminants have not yet been directly proven for any other organic chemical. Even though laboratory tests of mammals have shown that many toxic chemicals result in carcinogenic, mutagenic or teratogenic effects at sub-lethal doses, it is still extremely difficult to prove that there is a relationship between these illnesses in stressed ecosystems and the toxic organic chemicals found in them. The whole subject of what should be measured to assess ecosystem health increasingly needs to be examined. The PAHs are an interesting example. They are metabolized in higher organisms, and thus do not bioaccumulate as do DDT and HCB. However, the toxic metabolites of PAHs do bioaccumulate.

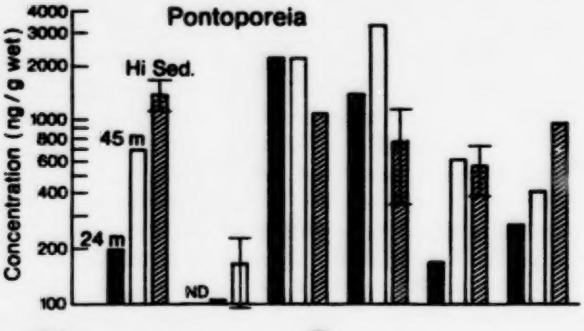

**Figure 11.** PAH concentrations (log scale) in amphipods (*Pontoporeia*), lake bottom sediments and pore water at progressively deeper sites (24-, 45-, 60-m depth offshore from Grand Haven) in southeastern Lake Michigan (after Eadie *et al.*, 1983). Ph – phenanthrene; An – anthracene; Fl – fluoranthene; Py – pyrene; Ch – chrysene; BaP – benzo (a) pyrene; Hi Sed. – 60-m depth, high sedimentation site.

In summary, the literature clearly documents that a variety of organisms that live in or come in contact with contaminated sediment bioaccumulate chemicals from

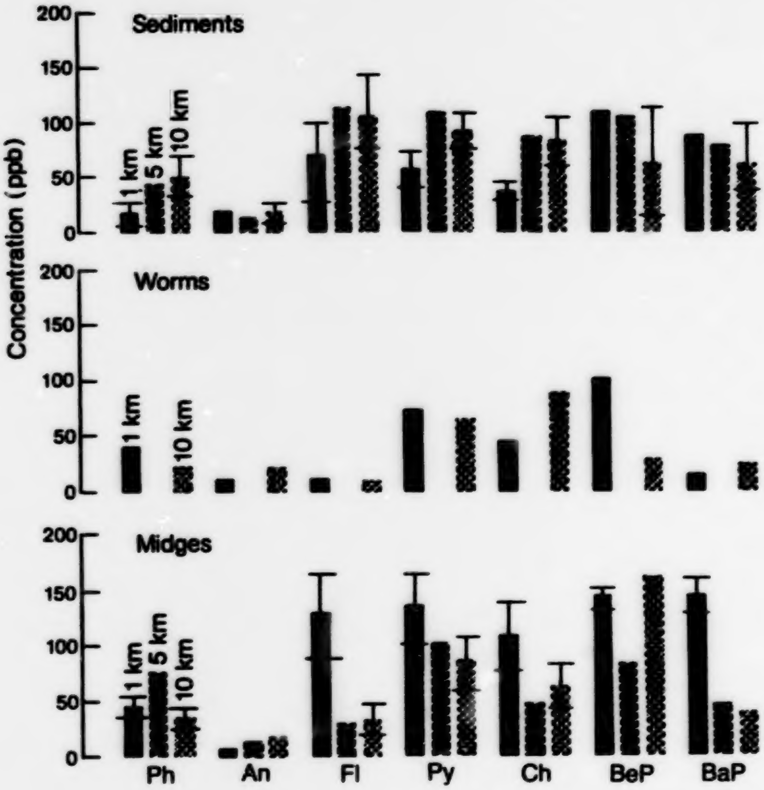

**Figure 12.** Concentrations of individual PAHs in lake bottom sediments, worms and midges in the Western Basin of Lake Erie, 1, 5 and 10 km from the Detroit Edison Monroe Power Plant in southeastern Michigan (1 and 10 km only for oligochaete worms). The bar represents one standard deviation (after Eadie *et al*., 1983). BeP — Benzo (e) pyrene. See Figure 11 for other abbreviations.

them. Thus, a fraction of the sediment contaminant load is definitely bioavailable. The laboratory tests of bio-uptake discussed above show that at least the following factors affect the bioaccumulation of sediment-associated, bioavailable, organic chemicals:

(a) Toxic chemical structure
(b) Organism size
(c) Duration of exposure of the biota to the sediments
(d) Chemical concentration in the sediments
(e) Sediment characteristics, especially organic content and particle size.

Thus, general principles that are the basis for future research have been determined through experimentation. Given the diversity of organisms, chemical structures, and sediment types, however, experiments of the type described above could be continued indefinitely. A more worthwhile approach may be to determine specific processes and rates of bioaccumulation for specific polluted environments, where the factors are unique but quantifiable. Such results may then be more useful in terms of general principles but also valuable in terms of improvement in ecosystem health monitoring and chemical control actions in specific polluted aquatic ecosystems.

# Biological Recycling of Particulate-Associated Contaminants

The importance of benthic organisms in the passage of sediment-associated organic contaminants up the food chain is related to the ability to rework contaminated surficial sediments. Much of this research has involved interpretation of historical contaminant loadings of contaminants to lakes as recorded in lake sediment cores (Fisher *et al*., 1980; Robbins, 1982). Robbins (1982) noted that an event resulting in contaminant deposition 20 years ago, in unmixed sediments, would have left a residue buried by about 25 cm of sediment and therefore out of contact with the water for all practical purposes. Yet as a result of bioturbation the contaminant concentration would decrease exponentially toward the sediment surface, and significant levels could remain in contact with water. This has important implications in terms of bioavailability, bioaccumulation and long-term fate of most toxic metals and hydrophobic organic contaminants in aquatic ecosystems.

In the Great Lakes, numbers of worms (*Tubifex tubifex*) can be as high as 100 000/m$^2$ of bottom sediment area. Fisher *et al*. (1980) studied these worms in laboratory tests using sediments with spiked contaminants. The tubificids mixed the sediment to depths of 6 to 9 cm. Feeding alone, over and above burrowing, caused considerable reworking of surficial bottom sediments. Tubificids ingest sediment at depth and expel it at the sediment water interface and thus act as conveyor belts returning sedimented and buried contaminants to the sediment/water interface. *Tubifex tubifex* feeds at depths of 0 to 10 cm in bottom sediment but most feeding is in a narrow zone of 5- to 8-cm depth. Thus a contaminated surface layer will be buried by further sedimentation as a unit until it enters the feeding zone when particles start to be returned to the sediment/water interface. Hence, unless there are very high sedimentation rates relative to bioturbation rates, considerable mixing occurs at the sediment/water interface. Weathering rates for sediment-bound oil have been studied in laboratory microcosms using marine-oligochaetes (*Arenicola marina*) (Gordon *et al*., 1978). The oil in the casts was found to be much lower (17% to 72%) than in the sediment. These marine worms are much larger than freshwater oligochaetes. They inhabit L-shaped burrows 20 to 40 cm long (Fig. 13). The sediment on which they feed comes from the surface, and they ingest particles up to 2 mm in size. Population densities are up to 100/m$^2$.

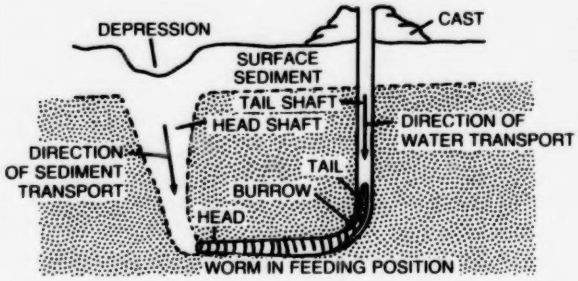

Figure 13. Schematic diagram of *Arenicola marina* burrow (not to scale). The strippled area denotes reduced sediment (after Gordon *et al*., 1978).

The principal benthic organisms in the Great Lakes are freshwater shrimps (*Mysis relicta*); amphipods (*Pontoporeia hoyi*); oligochaete worms (*Tubifex tubifex, Limnodrilus hoffmeisteri, Stylodrilus heringianus*); the midge larvae (*Chironomus anthracinus*); and freshwater clams (*Sphaerium* and *Pisidium* spp.). Concentrations of chemicals found in some of these bottom dwellers and in the bottom sediments of Lake Ontario are reported by Fox *et al*. (1983) (Table 1). For some organisms, there are good correlations between organism and sediment concentrations of organic chemicals but poor relationships for other associations (Fig. 14). Unlike the oligochaetes, the amphipods have a shallow (1- to 2-cm) penetration range into sediments and thus have an eddy-diffusive interaction with sediments as they plough randomly through these upper few centimetres of surficial sediment. Maximum mixing occurs in the deepest sedimentation basins of the Great Lakes where sediments are least consolidated. Bioturbation is thus a major post-sedimentation process affecting the fate of particle-associated toxic metals and persistent organic contaminants that are not primarily affected by volatilization, photolysis, or bio- and photo-degradation.

Sly (1983b) deduced that shallow water benthic species inhabit both the inner and outer parts of the Niagara Bar. Suspension feeders could accumulate toxic metals and organics from suspended particulates passing over the bar. In deeper water, the distribution of chironomids and oligochaetes coincided with the highest concentration of toxic

**Table 1. Concentrations of Organochlorine Contaminants in Surficial Sediments, Benthos and Fish from Sites in Lake Ontario near the Niagara River Mouth and One Reference Site in the Western Basin**

| Compartment | Concentration of organochlorine contaminants ng/g (dry weight) | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1,3-DCB | | 1,4-DCB | | 1,2-DCB | | 1,3,5-TCB | | 1,2,4-TCB | | 1,2,3-TCB | | HCBD | | 1,2,4,5-TeCB | | 1,2,3,4-TeCB | | QCB | | HCB | | PCBs | |
| | April | July | April | July | April | July | April | July | April | July | April | July | April | July | April | July | April | July | April | July | April | July | April | July |
| Sediment | NA | ND | NA | 33 | NA | 7.0 | NA | 14 | NA | 72 | NA | 7.2 | NA | 12 | NA | 36 | NA | 31 | NA | 26 | NA | 62 | NA | 730 |
| Oligochaetes | ND | ND | ND | ND | ND | ND | ND | ND | ND | 81 | ND | 1.3 | ND | ND | ND | 63 | ND | 25 | 48 | 38 | 69 | 140 | 1 800 | 2 600 |
| Amphipods | 31 | ND | ND | ND | 18 | ND | 2.4 | 14 | 7.1 | 150 | 9.0 | 19 | 9.0 | 24 | 8.1 | 38 | 24 | 90 | 14 | 67 | 90 | 370 | 2 600 | 6 600 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Sediment | 47 | 34 | 250 | 78 | 26 | 18 | 28 | 21 | 89 | 59 | 14 | 7.6 | 21 | 13 | 69 | 47 | 39 | 23 | 31 | 30 | 73 | 120 | 260 | 380 |
| Oligochaetes | NA | ND | NA | ND | NA | ND | NA | 22 | NA | 45 | NA | 6.3 | NA | 11 | NA | 21 | NA | 21 | NA | 41 | NA | 181 | NA | 930 |
| Amphipods | 41 | ND | 90 | ND | 8.1 | ND | 7.1 | 33 | 5.7 | 90 | 2.9 | 10 | 7.6 | 19 | 17 | 57 | 9.0 | 48 | 25 | 148 | 157 | 724 | 7 900 | 5 300 |
| Mysids | NS | ND | NS | ND | NS | ND | NS | 8.0 | NS | 13 | NS | 2.0 | NS | 6.0 | NS | 20 | NS | 19 | NS | 59 | NS | 96 | NS | 3 000 |
| Lake trout 1+ yr | NS | ND | NS | ND | NS | ND | NS | 1.0 | NS | 3.7 | NS | 0.3 | NS | 1.3 | NS | 4.0 | NS | 4.3 | NS | 14 | NS | 83 | NS | 6 300 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Sediment | 69 | 42 | 380 | 88 | 22 | 20 | 29 | 24 | 85 | 68 | 11 | 8.6 | 31 | 35 | 72 | 55 | 46 | 34 | 48 | 23 | 260 | 71 | 680 | 470 |
| Oligochaetes | 110 | ND | 630 | ND | 25 | ND | 60 | 39 | 20 | 63 | 9.3 | 7.5 | 37 | 13 | 53 | 75 | 20 | 19 | 28 | 69 | 63 | 230 | 1 400 | 1 400 |
| Amphipods | 27 | ND | 71 | ND | ND | ND | 20 | 140 | 20 | 330 | 6.7 | 29 | 8.6 | 57 | 33 | 210 | 13 | 130 | 35 | 420 | 190 | 1600 | 11 000 | 11 000 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Sediment | 73 | 47 | 290 | 90 | 24 | 18 | 27 | 26 | 75 | 70 | 9.0 | 10 | 21 | 20 | 58 | 61 | 32 | 31 | 59 | 32 | 230 | 110 | 840 | 810 |
| Oligochaetes | 75 | ND | 170 | ND | 31 | ND | 46 | 56 | 8.8 | 81 | 7.5 | 13 | 7.5 | 13 | 28 | 110 | 9.3 | 38 | 21 | 69 | 75 | 480 | 1 500 | 2 400 |
| Amphipods | 53 | ND | 90 | ND | ND | ND | 24 | 67 | 13 | 62 | 9.5 | 14 | 9.5 | 38 | 52 | 130 | 18 | 76 | 52 | 220 | 230 | 1200 | 4 700 | 17 000 |
| | | | | | | | | | | | | | | | | | | | | | | | | |
| Sediment | 170 | 42 | 1300 | 112 | 54 | 23 | 98 | 70 | 220 | 120 | 25 | 11 | 120 | 44 | 210 | 110 | 110 | 49 | 120 | 49 | 840 | 210 | 260 | 670 |
| Oligochaetes | 120 | ND | 510 | ND | 100 | ND | 69 | 75 | 34 | 69 | 11 | 6.3 | 19 | 28 | 110 | 110 | 69 | 42 | 81 | 81 | 270 | 1200 | 5 300 | 2 000 |
| Amphipods | 260 | ND | 370 | ND | ND | ND | 26 | 110 | 21 | 130 | 9.5 | 20 | 17 | 62 | 95 | 180 | 24 | 95 | 35 | 210 | 260 | 1400 | 5 300 | 5 200 |

NA – Not analyzed.
ND – Not detected.
NS – No sample.
After Fox *et al.* (1983).

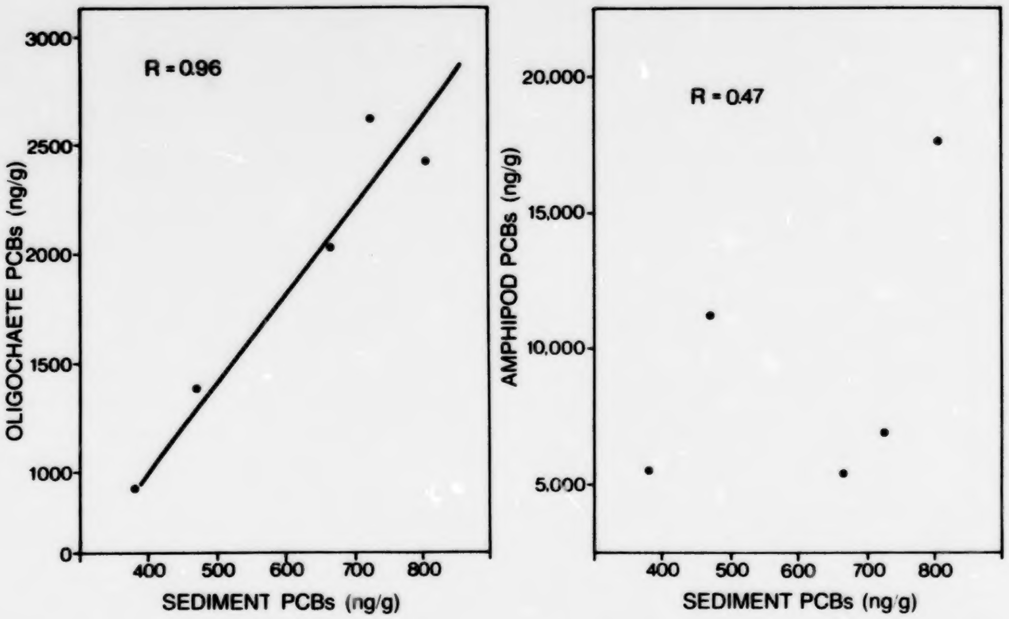

**Figure 14.** Oligochaete and amphipod PCB concentrations (dry weight) as a function of the corresponding surficial sediment PCB concentrations (dry weight) at five Lake Ontario sample sites in July 1981 (after Fox *et al.*, 1983).

metals in bottom sediments and thus also with toxic organics. The reason for this is that the same suspended particulates that transport contaminants are also the major transporters of organic carbon and bioavailable phosphorus.

If individual benthic organisms and chemicals are studied in controlled laboratory experiments, as mentioned earlier, some good but simple relationships can be observed, but these are usually of only limited value when applied to real aquatic ecosystems. Bioaccumulation to higher organisms is complex and affected by the inability of lower organisms and the ability of higher organisms to metabolize certain chemicals. Bioaccumulation is both chemical- and organism-specific in natural environments. The very complex real situation only becomes evident when a broad spectrum of chemicals and organisms is studied at specific polluted sites. It is clear from the Lake Ontario data (Table 1) that macrobenthos play an important role by accumulating bottom sediment-bound toxic organics and passing them on to predators. The densities of the two major benthic organisms usually analyzed are some 50 000/m$^2$ for oligochaetes and 1000/m$^2$ for amphipods in profundal zones of the Great Lakes (Robbins, 1982). Whittle and Fitzsimons (1983) determined concentrations of particulate-associated contaminants in amphipods from the east basin of Lake Erie, above the Niagara River, from Lake Ontario opposite the mouth of the Niagara River (Table 2), and from the eastern basin of Lake Ontario and found that concentrations in these organisms are considerably higher than the mean surficial bottom sediment concentrations of the same chemicals at the same locations.

**Table 2.** PCB and Organochlorine Concentrations in Amphipods (*Pontoporeia affinis*) from Lakes Erie and Ontario (ng/g) (ppb)

| Chemical | East Lake Erie mean | Western Basin (Niagara River mouth) Lake Ontario mean | Eastern Basin Lake Ontario mean |
|---|---|---|---|
| Total DDT | 110 | 440 | 1088 |
| PCBs | 560 | 1378 | 1849 |
| Mirex | ND | 228 | 41 |
| Dieldrin | 62 | 226 | 376 |

ND – Not detected; no mirex has been detected in Lake Erie bottom sediments.

After Whittle and Fitzsimons (1983).

Bacteria are an under-researched link in particulate/water interactions and related bioavailability of particulate-associated toxic organics. As in soils, many aquatic contaminant reactions in bottom sediments are bacteriologically controlled. Bacteria are the basic food of sediment detrivores and thus may be the first step in bio-uptake in the food web. As mentioned in Part I, bacteria in the water column usually pass through 0.45-μm filters and can thus be included in the "aqueous" phase. The relationship between octanol/water partition coefficients and sediment/

water partition coefficients, using organic matter as a normalizing function, may also be partly related to sediment bacterial populations and bacteria on the surface of particulate-organic complexes.

The physiological and ecological characteristics of an organism are also factors affecting bioaccumulation of contaminants from particulates. For example, oligochaetes are essentially lipid-like sponges. They ingest and/or absorb large quantities of organic chemicals. Increased natural organic content in sediment increases absorption of toxic organics but may simultaneously reduce the bioavailability of some chemicals. Oligotrophic lakes may thus have a greater bottom sediment bioavailable pool of toxic organics, which becomes reflected in higher levels of bioaccumulation than occurs in eutrophic lakes. Certain zooplankton excrete metals in feces as organic complexes which are more bioavailable than the originally ingested element and similar processes may apply to toxic organics. Goerke *et al.* (1979) found large variations in bioaccumulation in the Weser Estuary and that bio-uptake was both species- and compound-specific. Although food chain biomagnification was suspected at higher trophic levels, the same was not clear at lower trophic levels. Whereas bioaccumulation of inorganic substances can be complicated by competing ions, bioaccumulation of toxic organic substances appears relatively simple. Rates of uptake and elimination can be measured in laboratories, but as shown later, usually only residue levels after specific periods of time are measured.

If uptake of toxic organics by aquatic organisms is directly from the water (bioconcentration), then the concentrations in organisms should be predictable from octanol/water partition coefficients. A good example of bioconcentration of soluble chemicals is the uptake of chlorophenols by freshwater leeches (Table 3). The importance of the benthic food pathway followed by subsequent biomagnification is a separate, much more complex, organism-controlled process. There is still debate on whether biomagnification or bioconcentration (Fig. 15) is the process by which higher aquatic organisms accumulate bioavailable toxic organic chemicals. Biomagnification has been the favoured pathway, but recently bioconcentration has been better recognized.

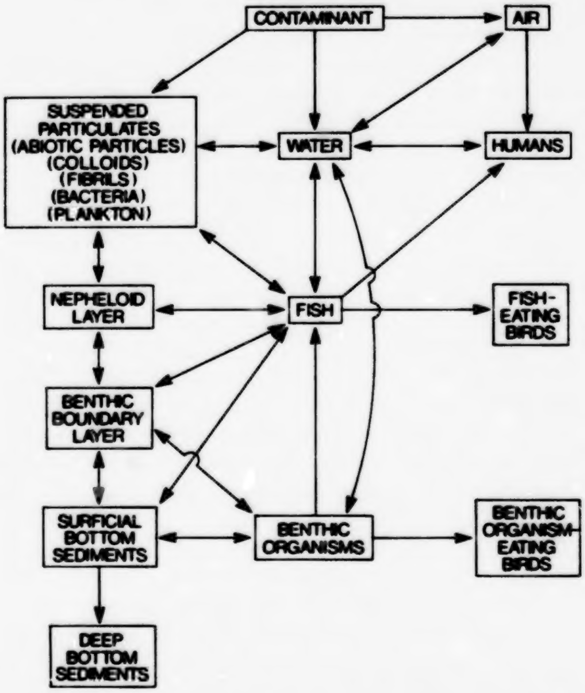
CONTAMINANT
AIR
SUSPENDED PARTICULATES (ABIOTIC PARTICLES) (COLLOIDS) (FIBRILS) (BACTERIA) (PLANKTON)
WATER
HUMANS
NEPHELOID LAYER
FISH
FISH-EATING BIRDS
BENTHIC BOUNDARY LAYER
SURFICIAL BOTTOM SEDIMENTS
BENTHIC ORGANISMS
BENTHIC ORGANISM-EATING BIRDS
DEEP BOTTOM SEDIMENTS

**Figure 15.** Freshwater pathways of bio-uptake of particulate-associated contaminants.

Bioconcentration may occur by direct exchange of chemicals from suspended particulates to gill surfaces, or by stripping of chemicals from particulates as they pass through digestive tracts. As mentioned before, abiotic and biotic par-

**Table 3. Chlorophenol Levels in Leeches and Water from Two Sites in Canagagigue Creek**

| Sample | Chlorophenol concentration (ppb) | | | |
|---|---|---|---|---|
| | 2,4,6-TCP | 2,4,5-TCP | 2,3,4,6-TTCP | PCP |
| Leech (*Dina dubia*) | 2201 | 10 262 | 508 | 188 |
| Leech (*Glossiphonia complanata*) | 639 | 1 688 | 100 | 19 |
| Leech (*Helobdella stagnalis*) | 371 | 2 461 | 140 | 72 |
| Water | 0.065 | 0.083 | 0.007 | 0.005 |
| | | | | |
| Leech (*Dina dubia*) | 1529 | 4 917 | 119 | 35 |
| Leech (*Glossiphonia complanata*) | 221 | 640 | 21 | 1 |
| Water | 0.014 | 0.015 | 0.003 | 0.003 |

After Metcalfe *et al.* (1984).

ticulates in a water column include a variety of materials: clays and other mineral particles with Fe/Mn or organic coatings, precipitated aggregations of minerals, colloidal precipitates, organics, phytoplankton, zooplankton, bacteria and fecal pellets. Phytoplankton and zooplankton are suspended aquatic particulates by "operational" definition because they are included in the material extracted by high-speed centrifuges or collected on filters. Fecal pellets are suspected to be one of the major sources of food for benthic scavengers. Biota can in fact be the dominant component of the "suspended particulate" load. Both phytoplankton and zooplankton are known to accumulate toxic organic chemicals to high enough concentrations to result in mortality and are commonly used as test organisms for metal and organic toxicity research. Plankton are essentially equivalent to living lipid globules. As such, they obey many of the octanol-water partitioning predictions for toxic organic chemicals. Plankton, at least non-carnivorous zooplankton, accumulate organic chemicals from the water, presumably by bioconcentration. In addition, however, plankton themselves are a major source of food. Many zooplankton feed on phytoplankton and other zooplankton. For higher organisms, especially many fish species, plankton can be a major particulate source of toxic chemicals. The effect of bio-uptake of toxic organic chemicals has been proposed as a cause of algae species composition shifts in some polluted ecosystems. In oligotrophic systems, where algal and zooplankton densities are much less, the food web is more attenuated. There is speculation that the same load of contaminants, added to an oligotrophic, as opposed to a eutrophic system, eventually results in higher concentration in suspended biotic particulates. Most complex phytoplankton and zooplankton research has been conducted as part of eutrophication studies and has focused on documenting shifts in species composition and densities as functions of various nutrient and other trace element concentrations and/or processes that affect productivity. Such research has not been extensive in the more analytically complex, toxic chemicals area, which has remained largely on a geochemical, chemical, or even standard water quality basis. The complexity of aquatic pathways of toxic contaminants and the possible role of biotic particulates in the water column result in a renewed need for extensive phyto- and zooplankton research combining different trophic level effects with contaminant bioconcentration and biomagnification processes in laboratory settings, limnocorrals, whole lake experiments, and polluted aquatic ecosystems.

# Physical Recycling of Particulate-Associated Contaminants

Physical recycling of particulates is a very significant part of all contaminant fate research. Relevant physical-particulate processes include

(a) Bottom sediment resuspension in rivers or lakes
(b) Bedload transport
(c) Sedimentation rates and processes
(d) Sediment circulation patterns in large lakes
(e) Nearshore erosion in lakes and impoundments
(f) Erosion downstream from reservoirs
(g) Dune formation and movements.

A variety of physical forces, such as the Coriolis force in large lakes, wind-generated waves or currents, and hydraulic processes such as under-ice suspended particulate transport, are all critical to an understanding of suspended particulate production and transport, and thus of the role of particulates in contaminant fate.

River discharge is a critical parameter, and event sampling and analyses must be done on the basis of a detailed knowledge of discharge and time of travel. Turk (1980) provides the example of PCB concentrations in relation to discharge in the severely contaminated Hudson River. A uniform and continuous release of PCBs from bottom sediment to the overlying water occurs in the Hudson River. At lower than median discharges, PCB concentrations rise as discharge falls. At higher than median flows, they rise as discharge increases (Fig. 16). The same general pattern occurs with Hg concentrations versus flow in the Wabigoon River of northwestern Ontario. In both of these cases, as river discharge decreases, dilution is less and concentration rises. Alternatively, as discharge rises, bottom sediments are resuspended and "whole water" concentrations rise. The relationships between rising flow and contaminant transport versus declining flow and sedimentation-storage need to be quantified. In small shallow lakes, wind-driven physical resuspension of bottom sediment is well known. In large lakes, however, the presence of resuspended sediments in deep basins has been discovered only recently. Lake Ontario is perhaps the best-documented example (Sandilands and Mudroch, 1983). The ultimate fate of contaminants in such large lakes is closely tied to the ultimate fate of these resuspended particulates.

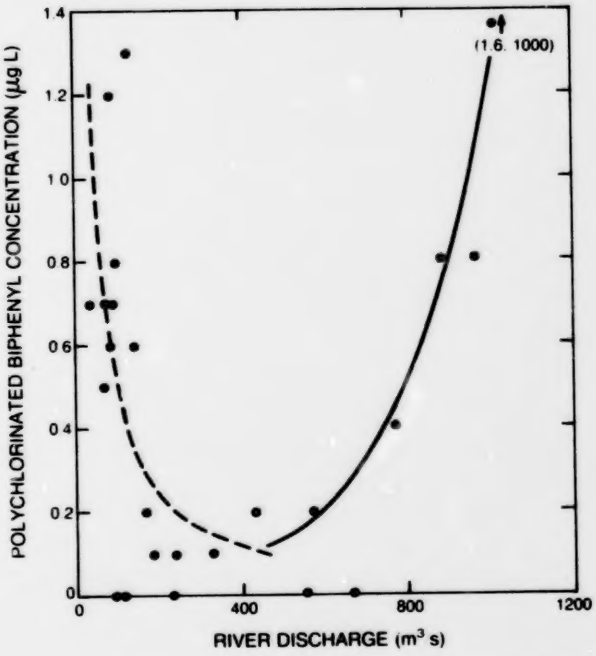

**Figure 16.** Relation of PCB concentration to river discharge, Hudson River at Schuylerville (after Turk, 1980).

## RECYCLING OF ORGANO-METALS (Hg) IN THE WABIGOON RIVER SYSTEM

In mercury-polluted aquatic ecosystems, even when all point sources are removed, cycling of particulate-associated mercury is the major cause of slow recovery. In the mercury-polluted Wabigoon River of northwestern Ontario (Allan *et al.*, 1984) methyl-Hg load is related to flow (Fig. 17) and reaches high values at times of high flow because of resuspension and transport of contaminated bottom sediments. Methyl-Hg concentrations, however, remain relatively low in high-flow periods. The highest concentrations of this more toxic form of Hg occur in the low-flow summer months (Fig. 17). Although the total mercury concentrations in sediment cores are deep within the sediment

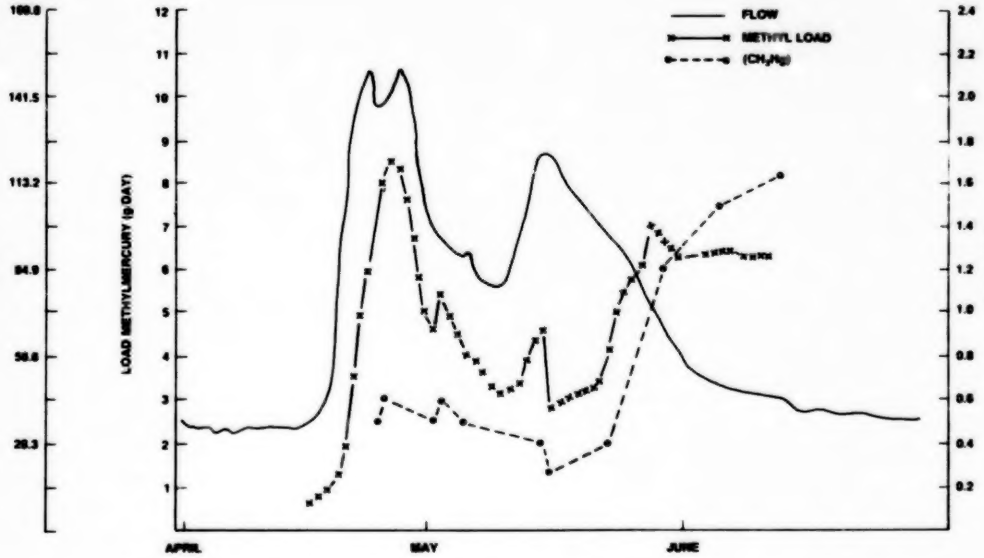

**Figure 17.** Methylmercury concentration loadings and flow data for the 1979 spring runoff, Clay Lake inflow, Wabigoon River (after Parks *et al.*, 1984).

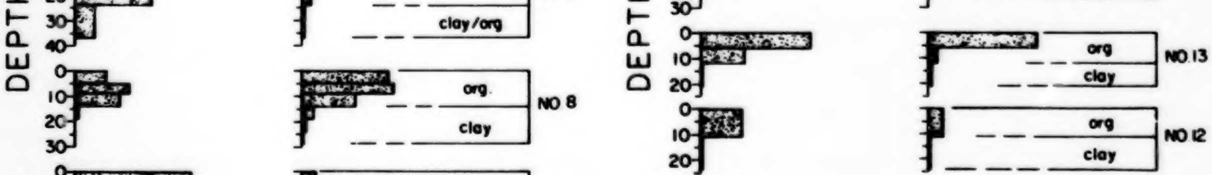

**Figure 18.** Total Hg and $CH_3Hg$ distribution in bottom sediment cores immediately downstream from Dryden (afer Jackson, 1980).

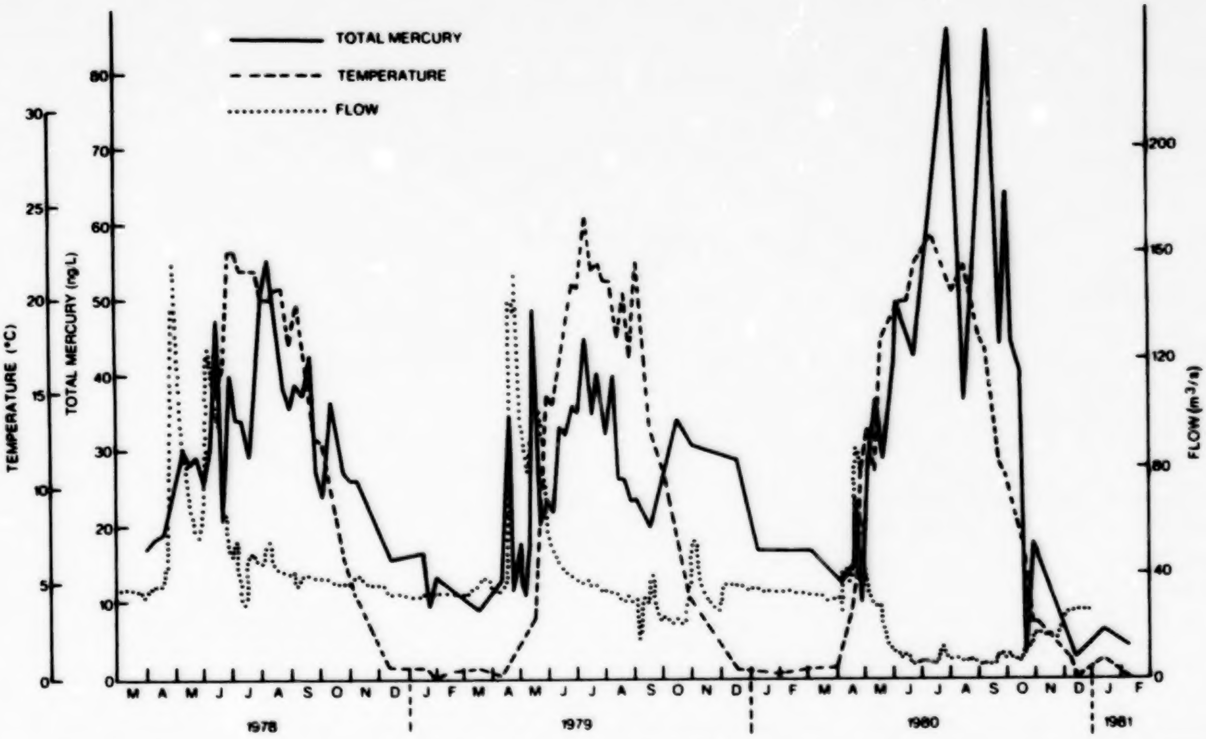

**Figure 19.** Total mercury and temperature data inflow to Clay Lake at Quibell, March 1979 to February 1981 (after Parks *et al.*, 1984).

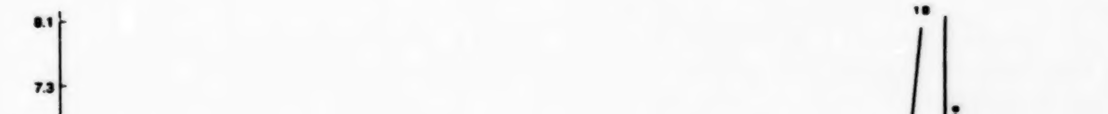

**Figure 20.** Methylmercury concentrations, Wabigoon River inflow to Clay Lake, March 1978 and November 1980 (after Parks, 1984).

profile at sites near the original source, methyl-Hg concentrations at these same sites are always highest in the surficial sediments (Fig. 18), thus ensuring recycling into the overlying water.

Over a three-year period, total mercury concentrations in the Wabigoon River were highest in the mid- and late summer months. The lower flows at this time could not account for the increased concentrations most closely correlated with water temperatures (Fig. 19). In 1980, total mercury in the water column exceeded 80 ng/L. Methyl-Hg concentration followed the same general pattern with maximum values in 1980 of some 18 ng/L (Fig. 20). There was a general correlation between methyl-Hg and total Hg throughout the river/lake system (Fig. 21). In the river stretches of the Wabigoon, regeneration of Hg from bottom sediments occurred by resuspension. In the lakes of the system, regeneration is evidenced by a buildup of methyl-Hg concentrations in hypolimnetic water (Fig. 22). Internal mercury and methyl-Hg regeneration have thus slowed the recovery of the Wabigoon River from Hg pollution.

An initial rapid drop in Hg concentrations in crayfish abdominal muscles (Fig. 23) was related to the removal of the point source input in 1970. More recently, slower declines are a result of recycling of bottom sediment-associated mercury. The initial rapid drop reflects the remarkable ability of a contaminated ecosystem to cleanse itself of persistent chemicals by their burial in lake and river bottom sediments, as discussed in Part I. Alternatively, the more recent slower declines in crayfish Hg concentrations show that a return to background conditions is retarded by recycling from the same bottom sediments. The predatory northern pike are at the top of the food web in the Wabigoon system. They also show a dramatic decline in mercury concentrations (Fig. 24). The lakes where the bottom sediment was most severely contaminated by mercury showed the most rapid improvements, but even after 12 years, internal regeneration of particulate-bound mercury still keeps concentrations well above those in northern pike from off-system lakes in the same area. Also, the lakes with the present highest surficial sediment mercury concentrations remain those in which northern pike have the highest mercury levels. Such relationships between selected biota and surface sediment total mercury concentrations (Fig. 25) indicate interaction between particulate-bound mercury and biota. The crayfish directly associated with suspended particulates have a higher mercury concentration than the pike at the top of the food web. Total Hg and, to a lesser extent, methyl-Hg in water show the same positive relation with mercury concentration in the same biota.

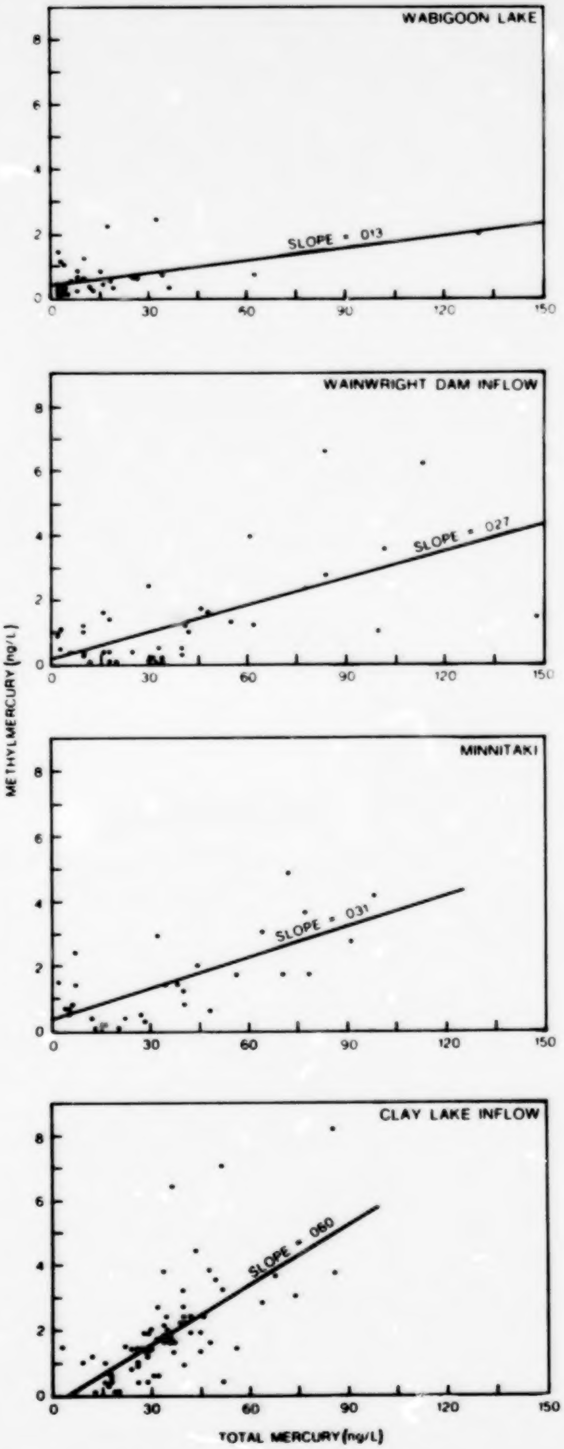

**Figure 21.** Relationship between methylmercury and total mercury at selected sites in the Wabigoon River system (after Parks *et al.*, 1984).

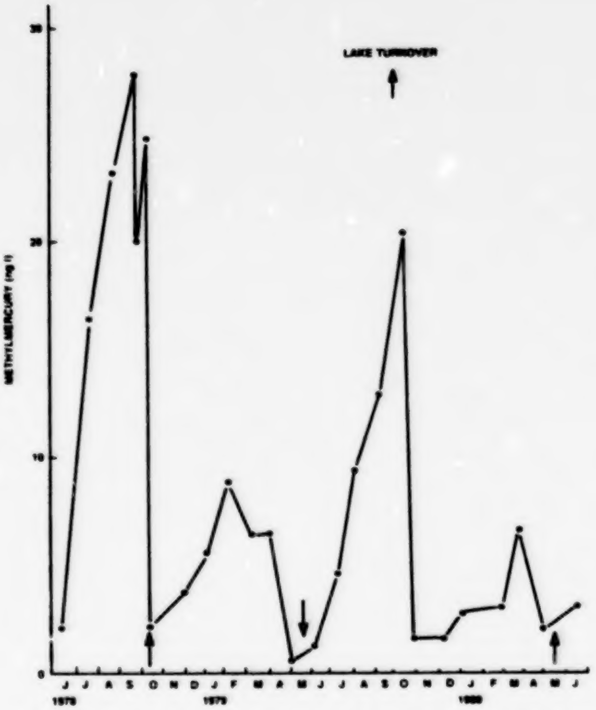

Figure 22. Methylmercury concentrations, western basin of Clay Lake, 1 m above bottom, June 1978 to June 1980 (after Parks *et al.*, 1984).

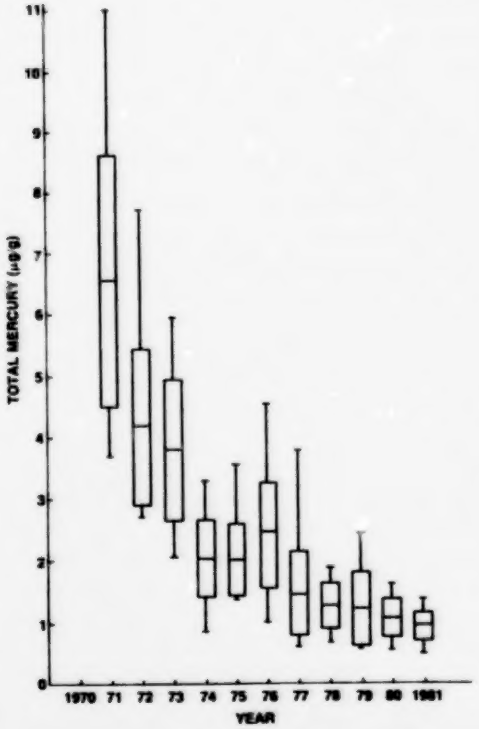

Figure 23. Mean, standard deviation and range of mercury concentrations in abdominal muscle of crayfish over 65 mm in total length, Clay Lake 1970–1981 (Allan *et al.*, 1984).

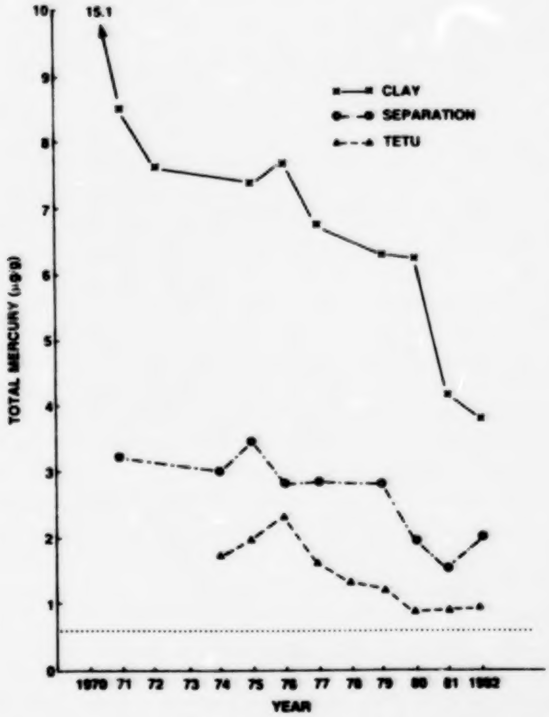

Figure 24. Mercury concentration in 60-cm northern pike from three lakes in the Wabigoon/English/Winnipeg River system 1971–82. Dotted line represents mean of four on system control sites (after Bishop and Neary in Allan *et al.*, 1984).

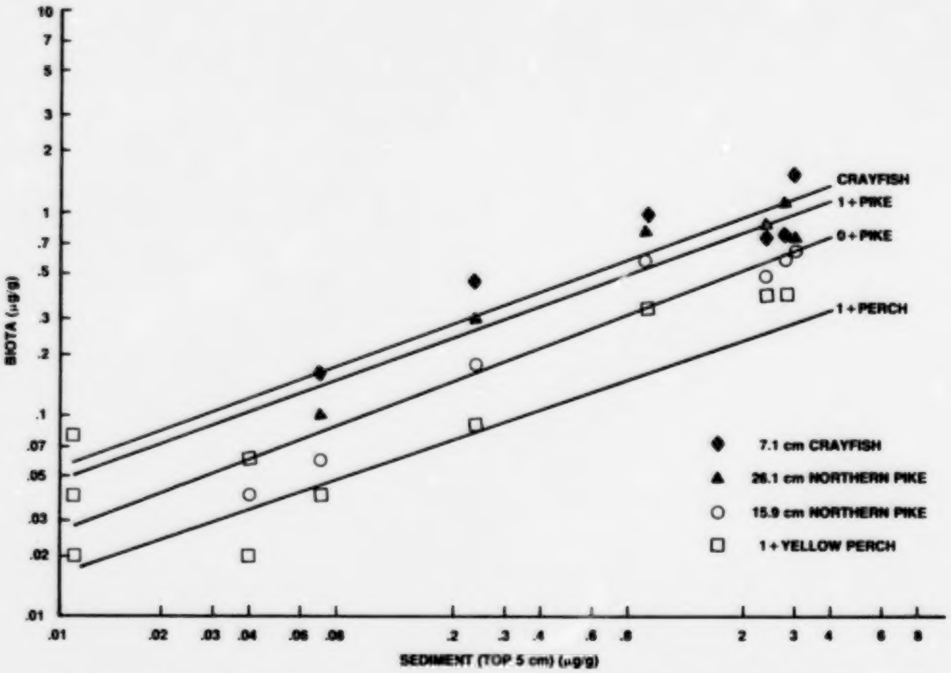

**Figure 25.** Relationship between total mercury concentrations in selected biota and in surface sediment, Wabigoon/English River system, 1979–81 (after Parks *et al.*, 1984).

## TOXIC ORGANIC CHEMICAL RECYCLING IN LAKE ONTARIO

Resuspension in large lakes, deep reservoirs and estuaries can produce dense cloud-like "nepheloid layers." Particulates in nepheloid layers consist of clay-size particles, biological debris, and aggregated particles. The initial investigation of a nepheloid layer in the Great Lakes was in Lake Michigan (Chambers *et al.*, 1980). The nepheloid layer had a thickness of about 10 m at the base of the offshore slope and gradually thinned farther offshore. In Lake Michigan, internal waves along the thermocline and wind-generated currents were considered the main forces that caused resuspension of particulates. The nepheloid layer increases with lake depth. Large amounts of bottom sediment-associated contaminants are resuspended into the overlying water. The lake water column is thus repeatedly re-exposed to previously sedimented contaminants, increasing the time required for permanent burial and removal from food webs. In 1982, a much thicker nepheloid layer than in Lake Michigan was first detected in Lake Ontario (Sandilands and Mudroch, 1983; Charlton, 1983). Transmissometer profiles (Fig. 26) at 94 stations in Lake Ontario revealed a turbid layer over the entire lake bottom at depths greater than 60 m. The thickness of the nepheloid layer in

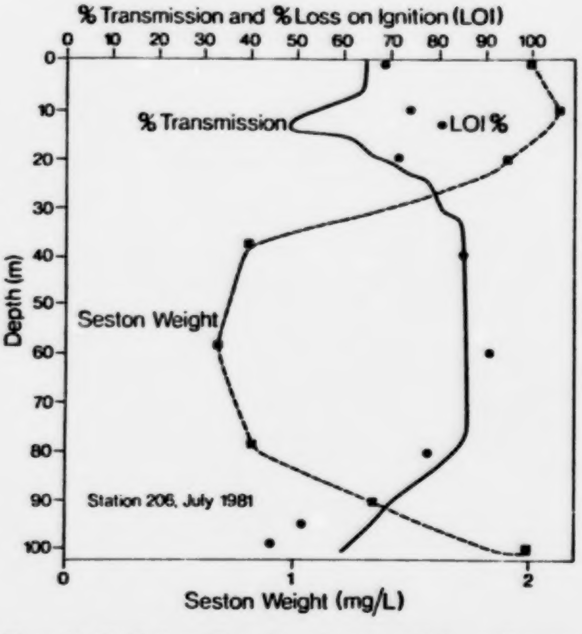

**Figure 26.** Vertical profiles of percent transmission and seston concentration (mg/L of dry weight and percent loss on ignition) (after Charlton, 1983).

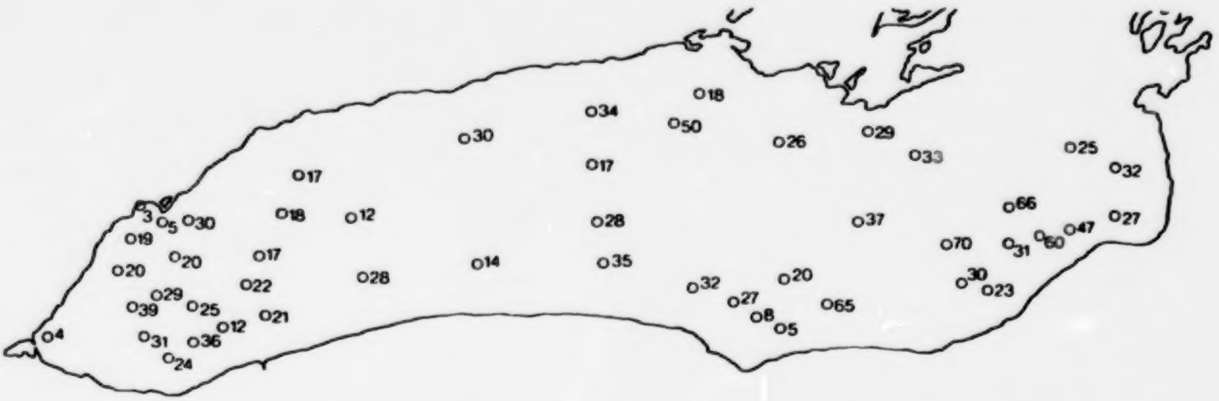

Figure 27. Thickness of the nepheloid layer (m) on August 10–14, 1981 (after Mudroch and Sandilands, 1983).

Lake Ontario on August 10 to 14, 1981, is shown in Figure 27 (Sandilands and Mudroch, 1983). The layer increased throughout the fall season. The discovery of this turbid layer in Lake Ontario led to a re-assessment of sediment resuspension as a significant long-term physical process of organic contaminant recycling in the lake. Charlton (1983) used arrays of suspended sediment traps (Fig. 28) to demonstrate the correlation between suspended particulate concentrations and transmissometer profiles. Contaminants may be desorbed from or ingested with some of the resuspended particulates. Alternatively, the particles in the nepheloid layer may provide an increased surface area for contaminant absorption, and this could even have positive aspects in terms of eventually increased sedimentation rates and more rapid burial of contaminants. In experiments in artificial lake simulators, Millard *et al.* (1983) found that PCBs could apparently be directly transferred from inorganic sediments to algae. However, the extent of direct biouptake of particulate-associated contaminants has not been clearly resolved. Sandilands and Mudroch (1983) found that the Pb and Zn concentrations in the suspended particulates in the nepheloid layer were the same as those found in bottom sediments at the same sites, whereas Hg, Cr, Co, Cu, As and Ni concentrations were less.

Oliver and Charlton (1984) investigated the relative contribution of organic contaminants in sedimenting (from the epilimnion) and resuspended (from the bottom) particles at different levels in the nepheloid layer. Sediment traps were used to collect sufficient particles for analyses. A significant fraction of the settling particulates in the deeper zones of Lake Ontario near the Niagara River and at all depths in the open lake was found to be resuspended bottom sediments. However, the biotic component of the particulates caught in the sediment traps resulted in poor correlations between sediment-water partition coefficients derived from the field data and those predicted on the basis of water solubility or octanol-water partition coefficients as determined for chlorobenzenes in laboratory tests.

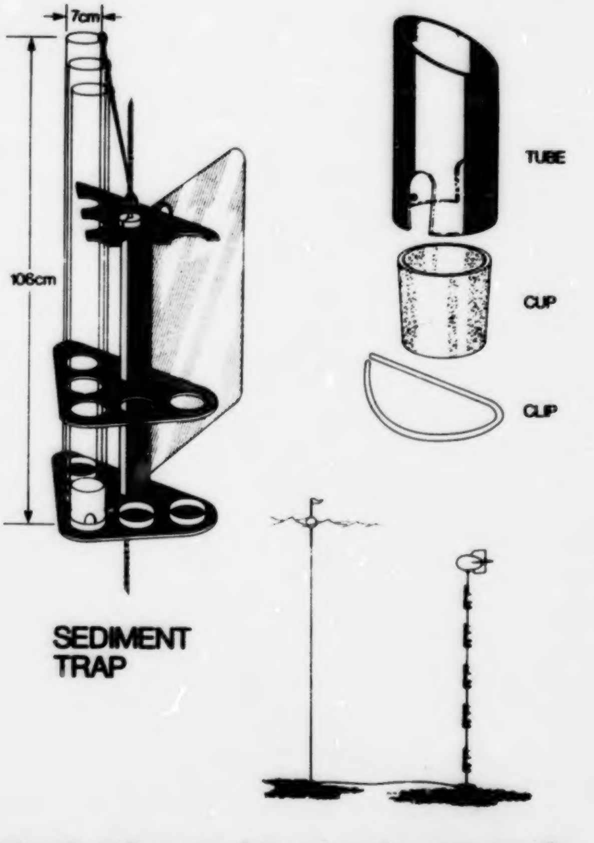

Figure 28. Sediment trap design and mooring arrangement (after Charlton, 1983).

The nepheloid layer in Lake Michigan (Chambers and Eadie, 1981) is formed during the time that the thermal bar is formed and then moves progressively offshore. Recent work has shown that during pronounced upwelling events, resuspended material can be reintroduced into nearshore areas. In large lakes such as Lake Ontario, there are periods when extreme wind stress can significantly tilt the thermocline so that the cold hypolimnetic water and the associated nepheloid layer are exposed on the windward shore (Fig. 29). Bottom sediment suspension may be considerable in winter when the lake is isothermal and currents penetrate deeply.

Contaminants may be bioconcentrated by ingestion of suspended particulates, organic-pollutant (colloidal/fibrilic) complexes, or contaminated food, or by passive sorption from particulate surfaces. In Lake Ontario and in other lakes, the major sources of particulate contaminant fluxes, excluding atmospheric sources, include sediments from inflowing rivers, sediments from shoreline erosion, resuspended bottom sediments and particulates produced in the lakes. Contaminants may be removed from organisms by secretion, including production of fibrils, molting or as feces. Bioconcentration of organic chemicals by zooplankton may result in high concentrations of the contaminants in their fecal pellets. On passage to the lake bottom, sinking fecal pellets may further scavenge hydrophobic pollutants. Varying amounts of different contaminants entering Lake Ontario are adsorbed to particulates to different degrees. Soluble contaminants entering the lake may be adsorbed to the increased suspended particulate loads derived from nearshore erosion or from bottom sediment resuspension, or by increased biological productivity. Most of these particulates are collected in sediment traps (Charlton, 1983).

At a 20-m depth in Lake Ontario, higher organic contaminant concentrations in particulates were observed at offshore than at nearshore stations, probably owing to bioaccumulation followed by settling of seston. When the downflux of chemicals was calculated from sediment trap catches, however, the effect of the Niagara River was very apparent. For example, HCB downfluxes were 8 ng/m$^2$/day versus 160 ng/m$^2$/day for offshore versus nearshore Niagara River inflow sites. In the open lake, there was considerable variation in contaminant downfluxes. Although many organochlorine contaminants were detected in the traps, the most prevalent were the chlorinated benzenes (CBs). The concentrations in the deeper traps were substantially elevated for PCBs, HCB and mirex, all of which are strongly partitioned onto bottom sediments. Oliver and Charlton (1984) were able to separate inputs from river detritus, resuspended bottom sediments and uncontaminated shoreline clays, by comparing the ratios of concentrations of various toxic organic chemicals in Niagara River suspended particulates and Lake Ontario surficial sediments with concentration ratios in particulates collected by sediment traps. Because sediment core analysis has shown that changes have occurred in chlorinated benzene isomer loadings in recent years, some ratios represent present input, whereas others represent resuspended bottom sediments. The expected resuspended sediment ratios were obtained by collecting cores, gently agitating them to produce a suspended cloud, and collecting and analyzing this resuspended material. Sediment trap particulates were collected at a station some 10 km from the mouth of the Niagara River. For some

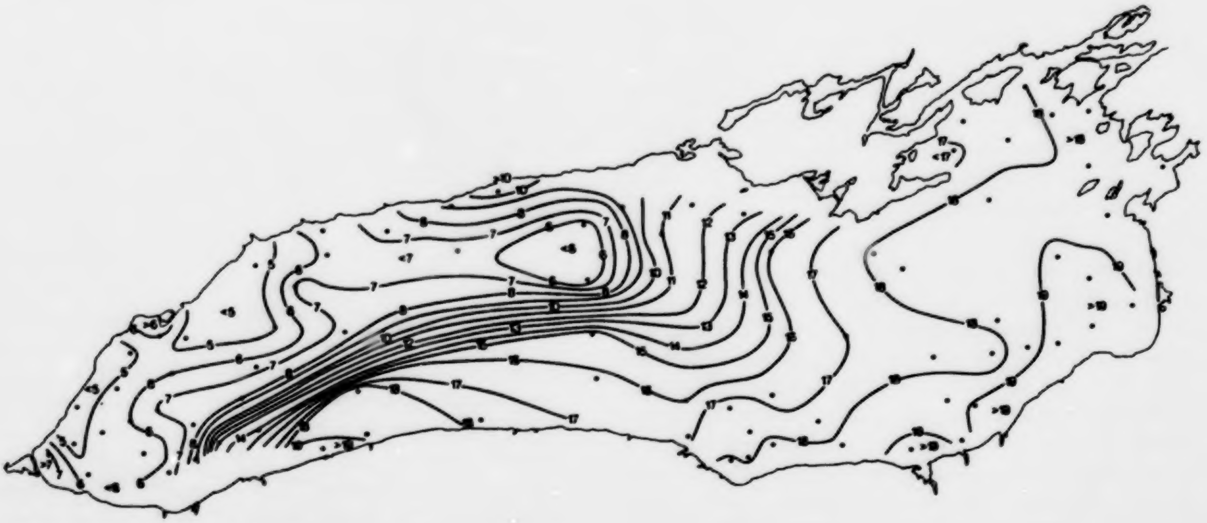

Figure 29. Lake Ontario: Temperature (°C) at a depth of 20 m, September 7-11, 1976 (after Dobson, 1984).

**Table 4. Selected Suspended Sediment, Organic Chemical Concentrations with Depth (ng/g)**

| Chemical | Depth in lake | | | Lake bottom sediments |
|---|---|---|---|---|
| | 20 m | 40 m | 68 m* | |
| PCB 40 | 1.4 | 2.7 | 2.8 | 23 |
| PCB 153 | 8.3 | 10.0 | 14.0 | 23 |
| PCT | 2.7 | 5.2 | 31 | 32 |
| Mirex | 12 | 19 | 50 | 48 |
| 1,2,4,5-TECB | 13 | 16 | 26 | 68 |
| 1,2,4-TECB | 38 | 36 | 48 | 110 |
| HCB | 31 | 35 | 96 | 110 |
| $\gamma$-BHC | ND | ND | 1.7 | 1.1 |

*2 m above the lake bottom.
After Oliver and Charlton (1984).

**Table 5. Percent Contaminant Contribution from Bottom Sediment Resuspension**

| Site | Depth (m) | Bottom sediment (%) |
|---|---|---|
| Near the Niagara River inflow | 20 | 0 |
| | 40 | 0 |
| | 60 | 22 |
| | 68 | 41 |
| Central Niagara Basin of Lake Ontario | 20 | 62 |
| | 40 | 57 |
| | 80 | 48 |
| | 90 | 70 |
| | 98 | 52 |

After Oliver and Charlton (1984).

chemicals, the particulates collected at depth had concentrations close to those in bottom sediments (Table 4) in the Niagara Basin of Lake Ontario. The amounts of settling particulates and their chemical concentrations permit calculation of net contaminant downfluxes. Many of the values, at least at the deeper locations, are in the hundreds of nanograms per square metre per day. Mirex was loaded to Lake Ontario by the Niagara River in the seventies. The production and use of mirex have been limited since 1976, and present day concentrations on suspended particulates in the Niagara River are very low. The high concentrations of mirex in many of the deeper, offshore, sediment traps are perhaps the best indicator of the continual physical recycling of contaminants by bottom sediment resuspension. Oliver and Charlton (1984) calculated percent contributions of bottom sediments to settling particles at different depths (Table 5). The percent contribution by bottom sediments was much higher in the middle of the lake, compared with the area influenced by direct input of suspended particulates from the Niagara River.

CHAPTER 6

# Bioaccumulation as an Indicator of Bioavailability of Particulate-Associated Contaminants

Concentrations of organic chemicals in biota provide insight into the degree of bioavailability of different chemicals. A long list of factors affect processes of bio-uptake, including temperature, light, dissolved oxygen content, other contaminant concentrations, time of exposure, food availability, number of species, predators, parasites and pathogens, clearance rates, body weight, adiposity and genetic composition. Few of these factors and parameters are ever measured along with contaminant concentrations, which means that most of the available data are only comparable on a very general, qualitative basis. Nevertheless, the literature contains many examples of environmental contaminant concentrations in biota and associated abiotic aquatic media, and such information is directly relevant to questions of particulate-associated contaminant bioavailability. Clearly, if contaminants are found in organisms that live in contaminated sediments or in association with contaminated suspended particulates, then there is proof of the degree of bioavailability of such chemicals. To investigate bioavailability and the related process of bioaccumulation, detailed information on interrelationships of the species present in an aquatic food web must be available or resolved by further study.

## BIOAVAILABILITY TO BENTHIC ORGANISMS AND PLANKTON

In Lake Ontario, deep water sites have the least number and diversity of benthic organisms (Nalepa and Thomas, 1976). In deep water, amphipods dominate the benthic community, constituting some 60% of the organisms present. The amphipods in the deeper water are *Pontoporeia affinis*, but in shallower water, *Gammarus fasciatus* dominates. Also, chironomids at the deeper water sites are found along with the oligochaete *Stylodrilus heringianus*, which replaces *Tubifex tubifex*, the more dominant oligochaete in intermediate depth water. The copepods *Limnocalanus macrurus* and *Senecella calanoides* spend part of their life cycle in bottom sediments. In the water column, the zooplankton population is dominated by the shrimp *Mysis relicta* (Carpenter *et al.*, 1974) which most of the day is at or slightly above the lake bottom, where it is in contact with the highest resuspended sediment concentrations in the nepheloid layer. In Lake Ontario, the maximum abundance occurs in August and was 113/m$^2$ in the central parts of the lake.

Understanding how contaminants, which appear to be primarily associated with particulates (sediments) in aquatic systems, are bioaccumulated into humans is often difficult for non-limnologists. Environmental scientists often hear the statement that "people don't eat sediments." Indirectly, however, people do eat sediments because many benthic organisms, for example, are directly exposed to contaminants in bottom sediment. These organisms are often part of several food webs leading up to humans. Bottom sediment biota exist at three trophic levels:

(a) Primary production by chemosynthetic bacteria

(b) Oligochaetes and chironomid detrivores and saprophytes

(c) Carnivorous chironomids and amphipods.

In Lake Ontario, the dominant worms are burrowing detrivores, which ingest "aged" material from 2- to 5-cm depth in the sediment (Gardner *et al.*, 1983). Chironomids are present both as detrivores and as predators. The detrivore chironomids usually ingest depositing suspended particulates, including fecal pellets, or newly deposited sediment close to the sediment/water interface. *Microspectra* sp. occurs in areas of high sedimentation rate. The dominant amphipod in Lake Ontario (*Pontoporeia affinis*) is a shallow burrower. The shrimp *Mysis relicta* derives a considerable portion of its diet by predation on biotic "particulates" (phytoplankton and small zooplankton). Gastropods are detrital feeders. Freshwater *Pelecypoda* are filter feeders. All of these benthic organisms, by various feeding habits, directly transmit particulate-associated contaminants into low levels of biotic food webs. Life cycles of benthic organisms affect their impact on food chains. Oligochaetes remain permanently in bottom sediments, whereas chironomids only inhabit bottom sediments as larvae and are redispersed in the adult stage. Amphipods go through a migratory phase and are capable of a rapid passive dispersal by currents. Mysids are involved in daily migrations from near the bottom sediment surface to relatively shallow depths (20 m) and are also transported passively and rapidly by currents. Sly (1983a) constructed a hypothetical food web for Lake Ontario, showing the connections between benthic organisms and fish which live in or near bottom sediments (Fig. 30). Lake trout from Lake Ontario have body burdens of organic chemicals, such as mirex and dioxin, which are highly partitioned to sediments. At least part of the bioaccumulation route for these chemicals is clearly from the bottom sediments and from suspended biotic and abiotic particulates. The more a fish species relies on benthic organisms as a food source, the more likely is bioaccumulation of sediment-associated hydrophobic organic contaminants, many of which are the more toxic by virtue of their chemical structures. Likewise, recovery of fish species from contamination is slowest for those that feed on benthic organisms or their predators.

A direct inverse relationship has been documented in laboratories between octanol/water partition coefficients and solubilities of organic chemicals in water. Bioconcentration by rainbow trout has been inversely related to chemical water solubility (Chiou *et al*., 1977) (Fig. 31). In Lake Ontario, Borgman and Whittle (1983) found that the log concentration of DDT in various biota was directly related to their log dry weight (Fig. 32). Transfer of organic contaminants to biota directly from suspended particulates has been demonstrated by Harding and Phillips (1978). Organic chemicals are sorbed across gill surfaces of fish. In any given environmental situation, it is thus critical to separate the suspended particulate fraction of contaminants from the so-called "soluble" fraction. Particulates play an important role in the bioavailability of PAHs. Bioconcentration of PAHs by zooplankton decreased with an increase in the fraction of the PAHs sorbed by particulates (McCarthy, 1983). For benthic organisms, bottom sediments and the associated pore water are major sources of PAHs to the food web. Sorption to humic particulates reduces biouptake of PAHs but possibly increases exposure time by maintaining the PAHs in the water column.

Concentrations in particulates of some hydrophobic organic chemicals can triple on passage downstream in the Niagara River, in spite of a doubling of the total suspended particulate load. The additional particulate material added in the river's course is mainly inorganic. The coarse fraction of the suspended particulates at the river mouth is biotic, namely phyto- and zooplankton-derived, probably from Lake Erie. This biotic material absorbs the chemicals and initiates their transfer to food webs. All of this occurs rapidly in the Niagara River proper before entry of the par-

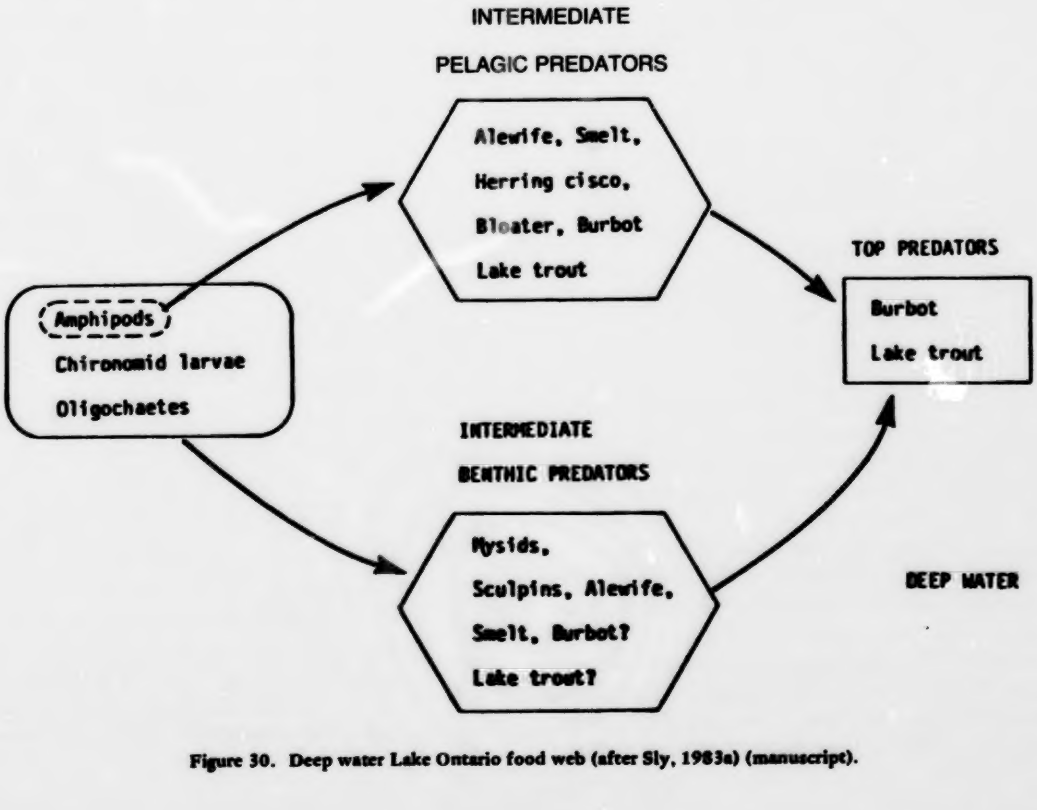

**Figure 30.** Deep water Lake Ontario food web (after Sly, 1983a) (manuscript).

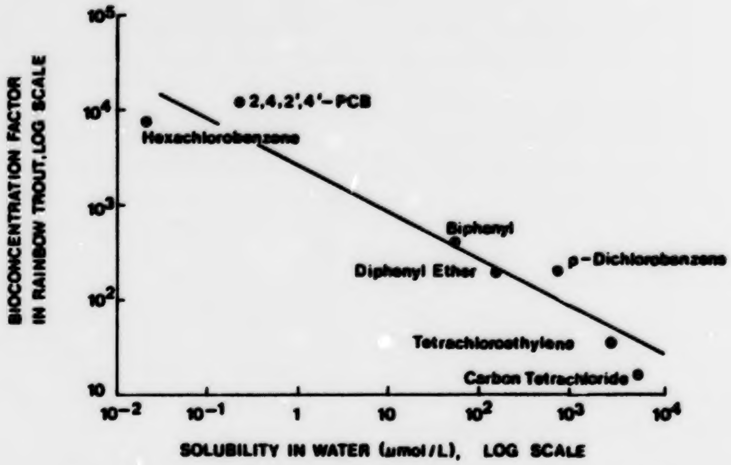

Figure 31. Lipophilicity and bioaccumulation (after Chiou *et al.*, 1977).

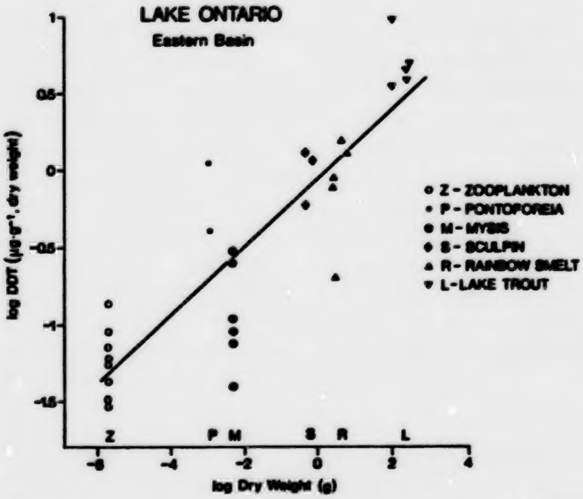

Figure 32. DDT concentrations as a function of body size (after Borgman and Whittle, 1983).

ticulates into Lake Ontario. The high-speed centrifuge systems described in Part I reduce these larger biotic particulates to an organic pulp which is analyzed as part of the suspended particulate load. Body fluids may pass into the effluent to be extracted by the APLE and referred to as aqueous phase, whereas their real transport mechanism is within biotic particulates. Fox *et al.* (1983) used plankton nets to separate biotic particulates in the Niagara River at Niagara-on-the-Lake, to avoid crushing of biota by filtration or centrifugation. The material collected was divided into six fractions (Table 6) from 75 to 700 μm by wet sieving and analyzed for CBs and PCBs. As an example of an extreme value, the 700-μm fraction at Niagara-on-the-Lake (NOTL) contained 11 ppm of total PCBs. Concentrations for several of the chlorobenzenes were in the hundreds of nanograms per gram (ppb). Many of the particulates were plankton, already part of the food web. A good correlation was found between sediment/water concentration ratios and the octanol/water partition coefficients for the compounds studied (Fig. 33), which implies that the organic fraction of the sediment dominated the partitioning. The suspended particulates were operating almost as lipid reservoirs. On passage into Lake Ontario these biotic particulates become involved in further partitioning, bioaccumulation, or biomagnification of toxic organic chemicals.

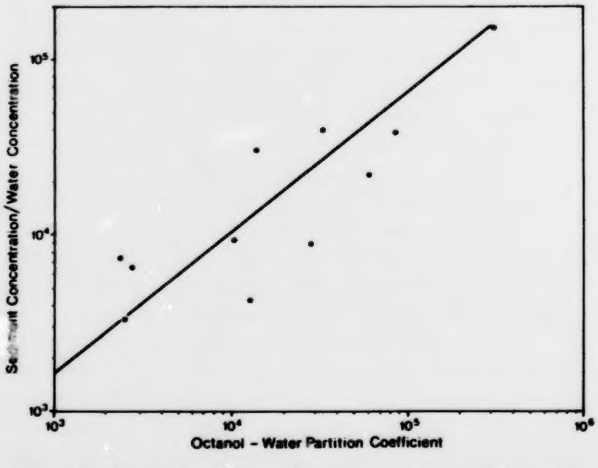

Figure 33. Log plot of the ratio, sediment concentrations (dry weight): Niagara River water concentration (13-sample average) for the compounds studied against the corresponding octanol-water partition coefficient (after Fox *et al.*, 1983).

**Table 6.** Concentrations of Organochlorine Contaminants in Size-Fractionated Suspended Particulates and Unfiltered Water from the Niagara River at Niagara-on-the-Lake (NOTL) and Fort Erie

| Niagara River suspended solids approximate size range and unfiltered water | Concentration of organochlorine contaminants (ng/g) (dry weight) (ng/L water) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1,3-DCB | | | 1,4-DCB | | | 1,2-DCB | | | 1,3,5-TCB | | | 1,2,4-TCB | | | 1,2,3-TCB | | |
| | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. |
| NOTL <75 μm | 42 | NS | 21 | 150 | NS | 96 | 38 | NS | 54 | 5.4 | NS | 1.5 | 50 | NS | 39 | 11 | NS | 5.4 |
| NOTL 75–175 μm | 27 | 20 | 73 | 97 | 300 | 250 | 36 | 35 | 110 | 3.1 | 4.0 | 4.4 | 37 | 33 | 110 | 12 | 4.4 | 15 |
| NOTL 175–300 μm | 190 | 43 | 120 | 440 | 680 | 330 | 65 | 64 | 106 | 5.8 | 7.8 | 13 | 121 | 97 | 150 | 21 | 12 | 22 |
| NOTL 300–500 μm | 81 | ND | 47 | 410 | 500 | 140 | 69 | 66 | 77 | 7.5 | 4.3 | 17 | 97 | 70 | 110 | 15 | 9.8 | 15 |
| NOTL 500–700 μm | 85 | ND | 47 | 380 | 220 | 300 | 72 | 53 | 110 | 3.8 | ND | 23 | 146 | 70 | 67 | 21 | 15 | 10 |
| NOTL >700 μm | 200 | ND | ND | 480 | 710 | 110 | 82 | 350 | 100 | 6.5 | ND | ND | 210 | 90 | 210 | 26 | 16 | 38 |
| Fort Erie >700 μm* | NS | ND | NS | NS | ND | NS | NS | ND | NS | NS | ND | NS | NS | ND | NS | NS | ND | NS |
| NOTL water | NS | 5.2 | NS | NS | 10.5 | NS | NS | 5.5 | NS | NS | 0.7 | NS | NS | 6.4 | NS | NS | 1.8 | NS |
| Fort Erie water | NS | ND | NS | NS | 1.0 | NS | NS | ND | NS | NS | ND | NS | NS | 0.1 | NS | NS | ND | NS |

| | HCBD | | | 1,2,4,5-TeCB | | | 1,2,3,4-TeCB | | | QCB | | | HCB | | | PCB's | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. | June | July | Sept. |
| NOTL <75 μm | 11 | NS | 8.2 | 27 | NS | 14 | 97 | NS | 29 | 38 | NS | 17 | 17 | NS | 15 | 640 | NS | 570 |
| NOTL 75–175 μm | 7.3 | 9.9 | 39 | 19 | 16 | 42 | 59 | 38 | 69 | 27 | 26 | 40 | 15 | 230 | 140 | 420 | 560 | 1 200 |
| NOTL 175–300 μm | 31 | 11 | 97 | 59 | 24 | 160 | 160 | 58 | 290 | 78 | 34 | 160 | 60 | 19 | 210 | 1400 | 580 | 770 |
| NOTL 300–500 μm | 33 | 36 | 28 | 81 | 26 | 74 | 320 | 86 | 150 | 170 | 110 | 400 | 68 | 97 | 460 | 1400 | 1700 | 3 700 |
| NOTL 500–700 μm | 230 | 9.6 | 27 | 45 | 19 | 110 | 130 | 56 | 130 | 70 | 40 | 64 | 48 | 180 | 37 | 1300 | 1700 | 5 400 |
| NOTL >700 μm | 710 | 37 | 28 | 97 | 51 | 120 | 320 | 300 | 120 | 220 | 270 | 100 | 92 | 89 | 58 | 5500 | 3800 | 11 000 |
| Fort Erie >700 μm* | NS | ND | NS | NS | ND | NS | NS | 6.0 | NS | NS | 3.0 | NS | NS | 5.0 | NS | NS | NA | NS |
| NOTL water | NS | 0.6 | NS | NS | 1.2 | NS | NS | 2.6 | NS | NS | 0.8 | NS | NS | 0.8 | NS | NS | 11.0 | NS |
| Fort Erie water | NS | ND | NS | NS | ND | NS | NS | 0.06 | NS | NS | 0.05 | NS | NS | 0.02 | NS | NS | NA | NS |

*Representative of all size fractions.
ND – Not detected.
NS – No sample.
NA – Not analyzed.
After Fox *et al.* (1983).

To understand fully the role of particulates in the biological fate of contaminants, estimates are required of the ranges in concentration of specific chemicals in all the various types of food to which different biota are exposed in aquatic ecosystems. Whittle and Fitzsimons (1983) determined concentrations of PCBs and other organochlorines in net plankton, Mysids and in smelt (Table 7). The concentrations in the netplankton are similar to those found in mysids, which spend at least part of the day close to or in contact with the bottom sediments and their resuspended component in the nepheloid layer. Thus contaminants which are extremely insoluble in water (but soluble in lipids), and are found almost exclusively in or on suspended and bottom particulates, are bioavailable to a considerable extent through their uptake by benthic organisms and planktonic particulates. Mirex and dioxin are the two best examples of this pathway in the Great Lakes. Mirex is present in suspended particulates in the Niagara River at a mean concentration of some 12 ppb in 75% of the samples. Other well-documented examples described earlier are Kepone in the James River and PCBs in the Hudson River.

## BIOAVAILABILITY TO FISH

Water is a poor indicator of contamination because it provides only instantaneous measurements. Many persistent, toxic, organic chemicals have already been bioaccumulated to significant levels by the time analytical methods are developed to detect them in raw water. For example, fish seldom exceed 25 ng/kg (ppt) TCDD (tetrachlorodibenzo-para-dioxin). The predicted water concentration would be about $10^6$ less. Detection in water at such extreme concentrations is only now possible. Degradation, sedimentation and other removal processes must all be considered when selecting an adequate medium to assess ecosystem pollution. Fish or sediments, which have roughly the same TCDD concentration at polluted sites, are better indicators of pollution problems and trends. Organisms such as fish and fish-eating birds, which integrate short-term changes in exposure, provide a better measure of contamination (Fig. 34).

In Lake Ontario, the food sources of smelt (*Osmerus mordax*) (Heberger and House, 1974), based on their main (20%) stomach contents, are as follows:

(1) *Small smelt (<11 cm)*

Amphipods, 51%.

Mysids, 28%.

Crustacean zooplankton, 20%.

(2) *Medium smelt (11 to 16 cm)*

Amphipods, 40%.

Fish, 32%.

Mysids, 23%.

(3) *Large smelt (>16 cm)*

Sculpins (a benthic organism eater which ingests bottom sediment with food), other smaller smelt and alewives, 54%.

Amphipods, 22%.

Mysids, 21%.

Alewife (*Alosa pseudoharengus*) stomach contents, unlike those of smelt, did not change with fish size. The unweighted mean percent composition of alewife stomach contents was 81% crustacean zooplankton (55% copepods); 13% amphipods (*Pontoporeia affinis* and *Gammarus*); and

**Table 7. Comparative Mean Values for Organochlorine Insecticides and PCBs in Lake Ontario and Lake Erie Biota (ng/g [ppb] dry weight)**

| Sample medium and site | % Lipid | ΣDDT | Dieldrin | PCBs | Mirex |
|---|---|---|---|---|---|
| Surface netplankton | | | | | |
| Western Basin, Lake Ontario | 16.0 | 72 | 17 | 280 | ND |
| Eastern Basin, Lake Ontario | 13.3 | 63 | 19 | 110 | ND |
| Mysis | | | | | |
| Western Basin, Lake Ontario | 7.9 | 59 | 10 | 580 | ND |
| Eastern Basin, Lake Ontario | 3.9 | 79 | 17 | 150 | ND |
| Smelt | | | | | |
| Western Basin, Lake Ontario | 5.6 | 533 | 70 | 858 | 35 |
| Eastern Basin, Lake Ontario | 4.4 | 390 | 65 | 1000 | 50 |
| Eastern Basin, Lake Erie | 4.1 | 141 | NA | 207 | ND |

ND – Not detected.
NA – Not analyzed.
After Whittle and Fitzsimons (1983).

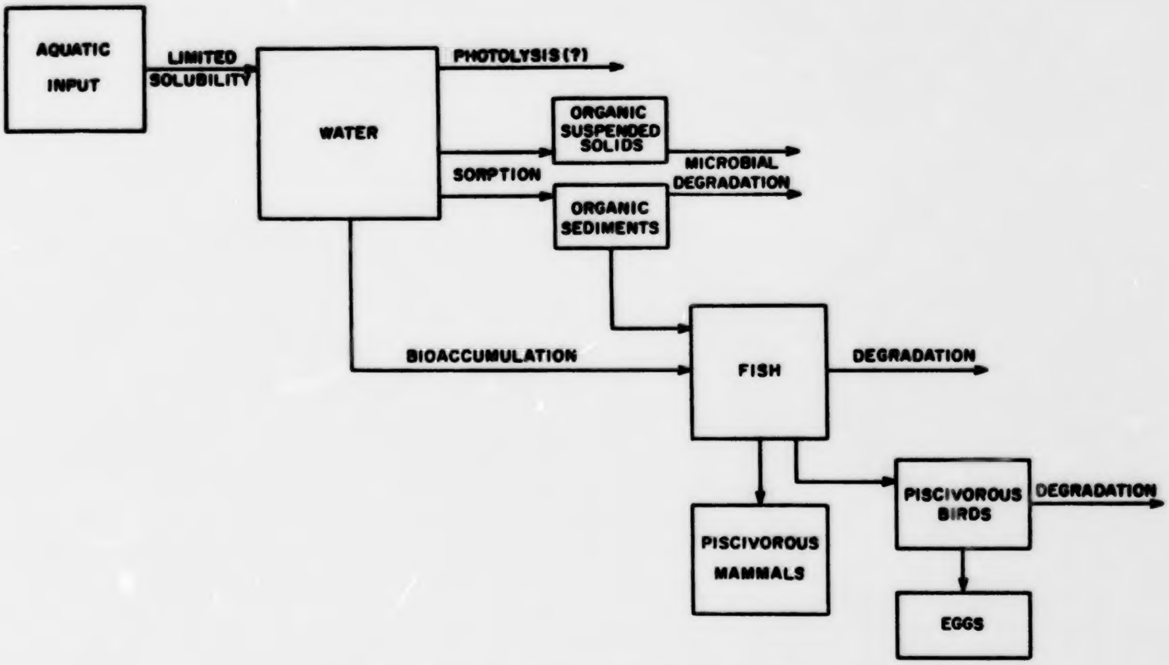

Figure 34. Aquatic bioaccumulation and degradation pathways.

4% mysids (*Mysis relicta*). In Lake Ontario, stomach contents of juvenile lake trout (*Salvelinus namaycush*) of 10 to 45 cm in length were analyzed by Elrod (1983). The fish were taken along the south shore of the lake where surficial sediment toxic chemical contamination is at a maximum. Lake trout inhabit the hypolimnion which at depth is actually the nepheloid layer. The availability of forage fish is strongly influenced by the thermal regime of the lake. For all seasons, the major forage fish (42% by weight) was the slimy sculpin (*Cottus cognatus*). In April and May, alewives made up 28% of the fish remains in stomachs. Rainbow smelt were the principal forage fish during the July/August period and constituted 25% of the fish remains. Amphipods (*Pontoporeia affinis*) and crustaceans (*Mysis relicta*) were also found in the trout stomachs. Invertebrates were a major diet of 15-cm lake trout in the April to May period. The stomach contents of Coho salmon largely consist of smelt and alewives (Norstrom *et al*., 1978).

Bioaccumulation data are extremely disjointed. For some chemicals several media have been analyzed but for others only one or two values, widely separated in terms of trophic level, are available. Many data are in unpublished United States federal and state and Canadian federal and provincial water quality data files. The data are seldom extensively interpreted in terms of chemical pathways or used in predictive models. Perhaps they cannot be so used. The data are collected primarily in response to bilateral water quality agreements and not to test critical hypotheses of toxic chemical pathways and fate. Strachan and Edwards (1984) have reviewed this data base and extracted as much meaningful information as possible for a large number of chemicals. For specific purposes, details of sample type, location, analytical procedures used, ranges in concentration, and other parameters are all important in terms of the meaning of each individual value. Very crude mean values, based on lumping of diverse values, simplify the disjointed data (Table 8) for a few selected chemicals, so that an overall picture of the ranges of concentration in various organisms and media becomes evident. Gaps in the data base and wide ranges in concentrations are usually related to the many ecosystem variables, critical in predictions of chemical fate but seldom recorded and more than likely never measured, including: water nutrient data at the sample site; organic content of bottom sediments; particle size densities of sediments and suspended particulates; benthic organism densities; benthic organic species composition; algae densities and species composition; zooplankton densities and species composition; fish species composition; fish size, age, lipid and stomach contents. Most data exist for the easily collected and analyzed media of bottom sediments and fish. Only scant data are available on intermediate food web biota such as benthic organisms and plankton (both phytoplankton and zooplankton). The data for suspended particulates are perhaps partly influenced by inclusion of biotic particles, but to what extent cannot be resolved. It is clear

Table 8. Summary and Range of Concentrations of Organic Contaminants in Lake Ontario Media (ppt or ng/kg [L])*

| Chemical | Raw water | Bottom sediment | Benthos | "Suspended" sediments | Plankton | Fishes | Herring gull eggs |
|---|---|---|---|---|---|---|---|
| Total DDT | 0.3–57 | 25 000–218 000 | 440 000–1 088 000 | 40 000 | 63 000–72 000 | 620 000–7 700 000 | 7 700 000–34 000 000 |
| PCBs | 5–60 | 110 000–1 600 000 | 470 000–9 000 000 | 600 000–6 000 000 | 110 000–6 100 000 | 1 378 000–17 000 000 | 41 000 000–204 000 000 |
| Mirex | 0.1 | 144 000 | 41 000–228 000 | 15 000 | ND–12 000 | 50 000–340 000 | 1 800 000–6 350 000 |
| CBs | 1–54 | 11 000–4 500 000 | NA | 574 000 | 27 000 | 6 000–370 000 | 300 000 |
| Dioxins | 0.01–0.03 | 8 000 | NA | NA | NA | 5–107 | 44–1 200 |
| Lindane | 0.4–11 | 46 000 | NA | 1 000–12 000 | 12 000 | 2 000–360 000 | 78 000 |

*These values are only of the crudest nature and are not statistical means. Where only one reference existed, the numbers are means, often of widely ranging values. Where a range is given, several sources of data were involved.

ND – Not detected.
NA – Not analyzed.

Compiled from Borgmann and Whittle (1983); Fox *et al.* (1983); Strachan and Edwards (1984); Weseloh (1983).

that suspended particulate, toxic organic chemical concentrations are very much higher than water concentrations, often $10^3$ to $10^6$ times higher than might be expected for hydrophobic and lipophilic compounds. The concentrations in netplankton, at least for PCBs and lindane, are not much higher than in the suspended "particulates," perhaps because some of the latter are actually centrifuged biota. With the exception of PCBs, concentrations are usually higher in bottom sediments than in suspended particulates. At this level of aggregation of data, however, with such wide ranges in concentrations, the values may be taken as essentially similar. All the chemicals, with the exception of lindane, are strongly partitioned to sediments, even when suspended particulate loads and the organic content are both low.

Trophic level may be important in terms of bioavailability and thus the eventual bioaccumulated concentrations resulting in fish at the top of a food web. Both Lakes Erie and Ontario receive high loads of several toxic organic chemicals of the type that associate with bottom sediments and particulates. High concentrations of several organic contaminants in suspended and bottom particulates occur in both Lakes Ontario and Erie. The former, however, is an oligotrophic lake, the latter eutrophic, and concentrations of most of the contaminants are higher in particulates from Lake Ontario. Coho salmon in Lake Erie also have lower concentrations of several of the same compounds relative to Lake Ontario (Fig. 35). One hypothesis is that a greater quantity of biotic particulates results in greater partitioning and lower concentrations both in the particulates and in the aqueous phase. Also, the total water column mass of a toxic organic chemical would be decreased by increased sedimentation rates in eutrophic situations. However, in shallow eutrophic lakes, there is usually more resuspension of bottom sediments, which in some situations may release contaminants to the aqueous phase by re-establishing new equilibria, or in other situations could reduce aqueous phase concentrations by adsorption. Nutrient–contaminant interactions require far greater study.

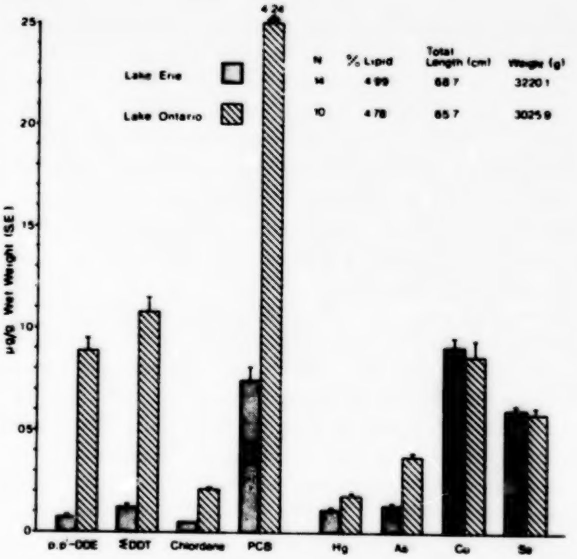

Figure 35. Comparative mean values for whole body contaminant burdens (μg/g wet weight) for 3⁺ aged Coho salmon (*Oncborbyncbus kisutcb*) from Lake Erie and Lake Ontario (after Whittle and Fitzsimons, 1983).

Borgmann and Whittle (1983) collected zooplankton, benthic amphipods (*Pontoporeia affinis*), mysids (*Mysis relicta*), slimy sculpins, rainbow smelt, lake trout and Coho salmon in the eastern and western basins of Lake Ontario. They assumed that contaminants were accumulated primarily from food rather than from water. Amphipods are an important food source for sculpins, which are benthic organisms, and sculpins are an important food source for lake trout. Association with contaminated bottom sediments results in higher toxic organic concentrations in amphipods (Table 9), which pass on these concentrations to sculpins, which have higher concentrations than might be predicted from their size. Lake trout have higher concentrations than salmon, possibly because they feed on sculpins

Table 9. Mean Size and Contaminant Concentration (dry weight basis) for Organisms from the Eastern and Western Basins of Lake Ontario (ppb [ng/g])*

| Organism | Body weight (g) | PCBs |  | Total DDT |  |
|---|---|---|---|---|---|
|  |  | E. basin | W. basin | E. basin | W. basin |
| Zooplankton | $2 \times 10^{-6}$ | 200 | 310 | 60 | 80 |
| Amphipods | $1.3 \times 10^{-3}$ | 1 700 | 1 670 | 690 | 480 |
| Mysids | $5.3 \times 10^{-3}$ | 290 | 390 | 120 | 280 |
| Sculpins | 0.66 | 3 820 | – | 970 | – |
| Smelt | 4.2 | 2 380 | 6 750 | 780 | 2200 |
| Lake trout | 246 | 14 100 | 20 700 | 4920 | 5700 |
| Coho salmon | 434 | – | 9 140 | – | 3260 |

*Numbers of samples: 20 and 4 for zooplankton; 8 and 4 for amphipods; 12 and 41 for mysids, and over 50 for all three fish in the Eastern and Western basins, respectively.
After Borgmann and Whittle (1983).

but also perhaps because of age. The mysid concentrations were considered low, but this was attributed to lipid release from these fragile organisms prior to analysis. Contaminant concentrations were generally related to body size rather than lipid levels. Borgmann and Whittle (1983) developed a concept of particle size conversion (PSC) efficiency for contaminants, based on the log of the amount of contaminant consumed divided by the amount retained (not metabolized or excreted); divided by the log of the predator size divided by the size of the prey. A measure is provided of the efficiency with which a contaminant is retained from one size organism to another. High retention of a contaminant gives a low (PSC) value. Combined with known values of particle size conversion, equations can be used to predict contaminant concentrations at one trophic level from knowledge of concentrations at another level. Such equations based on known contaminant concentrations in biota are important aspects of predictive models and could link particulate-associated contaminants to levels of the same contaminant in top predators.

Declining contaminant levels in fish are a clear indication of cut-off of sources or removal of contaminants by burial in bottom sediments, volatilization, degradation, and dilution downstream. Polychlorinated biphenyl concentrations in fish in the Hudson River have recently declined (Armstrong and Sloan, 1980), but this could be related to the recent lack of high flows needed to resuspend the contaminated bottom sediments. In Lake Ontario, PCBs in most fish have declined, although trends are not at all clear probably owing to several processes including airborne input of PCBs and complex internal recycling of residual contamination. For Chinook and Coho salmon, a decline of some 46% in PCB levels occurred between the mid-1970s and 1978. For mirex (Table 10) the trends are similar to those for PCBs. Whittle and Fitzsimons (1983) reported a mean concentration of 3.8 ppm (µg/g) PCBs in lake trout from Lake Ontario and several of the salmonids in Lake Ontario still exceed the FDA (United States Food and Drug Administration) guideline for human consumption. Mean concentrations of mirex in lake trout were 0.13 to 0.15 ppm in Lake Ontario. Declines in mirex concentrations are slow and many adult salmonids exceed the FDA guideline for human consumption. By 1980, there was no longer a clear decline in mirex or PCBs. In 1980, dieldrin concentrations in salmonids appeared to increase, as did those of HCB and chlordane. A decline in DDT has occurred from 1970 to 1980 in Lake Ontario fish. The slow recovery of the lake from pollution by these chemicals is clearly due in part to recycling of particulate-associated contaminants.

Table 10. Mirex Concentrations in Lake Ontario Fish (standard fillet sample)

| Species | Origin | Total mirex (ppm) and number of fish 1976 | 1977 | 1978 |
|---|---|---|---|---|
| Rainbow trout | Lake | 0.05 | 0.17 | – |
| Brown trout | Lake | 0.09 | 0.16 | 0.11 |
| Lake trout | Lake | 0.22 | 0.24 | 0.35 |
| White perch | West of Oswego River* | 0.11 | 0.16 | 0.14 |
| White perch | Oswego River and east | 0.04 | 0.14 | 0.13 |
| Smallmouth bass | West of Oswego River | 0.12 | 0.36 | – |
| Smallmouth bass | Oswego River and east | 0.10 | 0.29 | – |

*Oswego River was the second major source of mirex to Lake Ontario, after the Niagara River.

After Armstrong and Sloan (1980).

Benthic organisms are the main food source of spottail shiners (*Notropis hudsonius*) in nearshore areas of the Niagara River. These fish also consume suspended particulates (zooplankton and phytoplankton). Spottail shiners may thus indicate the bioavailability of particulate-associated contaminants in suspended particulates by a direct exposure route, and in bottom sediments by the indirect benthic organism route.

In 1981, a 20-m bag-sieve of 0.6-cm mesh was used to collect spottail shiners at seven nearshore locations in the Niagara River. Total DDT, PCBs, mirex and 2-4 DCB concentrations (Fig. 36) can be compared with concentrations in bottom sediments, resuspended particulates, benthos, plankton and water analyses given elsewhere in this review. Suns *et al*. (1983) also analyzed young-of-the-year (about 5-cm length) spottails in 1981 for the same chemicals and for dioxins (Fig. 37). Juvenile spottails were used because they have low mobility. There is, however, a limit to the use of spottails, because they are absent if contamination is too severe. At Niagara-on-the-Lake, mean levels of contaminants in spottails had declined as follows:

| | |
|---|---|
| Total DDT: | 244 ppb (1975); 157 ppb (1977); 26 to 99 ppb (1978 to 1982) |
| PCBs: | 690 ppb (1975); 654 ppb (1977); 153 to 327 ppb (1978 to 1982). |

Recent (1978–1982) levels of DDE, PCBs (Fig. 38) and mirex (Fig. 39) are all lower than in 1975–1977. Mean concentrations in 1978–82 at Niagara-on-the-Lake were 264 ppb PCBs; 64 ppb total DDT; and 11 ppb mirex. Trends for chlorobenzene isomers in spottails from Niagara-on-the-Lake and eastern Lake Erie (Table 11) show that the higher chlorinated benzenes added to the Niagara River between Lake Erie and Lake Ontario are bioaccumulated to the parts per billion level in spottails even in the short (12 h) time of travel of water between Niagara Falls and Lake Ontario.

Table 11. Chlorobenzene Isomers in Young-of-the-Year Spottail Shiners (ppb [ng/g])*

| Chemical | Location |  |  |  |
|---|---|---|---|---|
|  |  | Niagara-on-the-Lake |  |  |
|  | Lake Erie | 1979 | 1980 | 1981 |
| 1,2,4-TCB | 2 | 7 | ND | ND |
| 1,2,3,5-TECD | ND | 4 | ND | ND |
| 1,2,3,4-TECB | ND | 27 | 3 | 4 |
| QCB | ND | 1 | 14 | 7 |
| HCB | TR | 11 | 10 | 5 |

*45 fish in three composite samples were analyzed to obtain the mean values.

ND – Not detected.
TR – Trace.

After Suns *et al.* (1981, 1983).

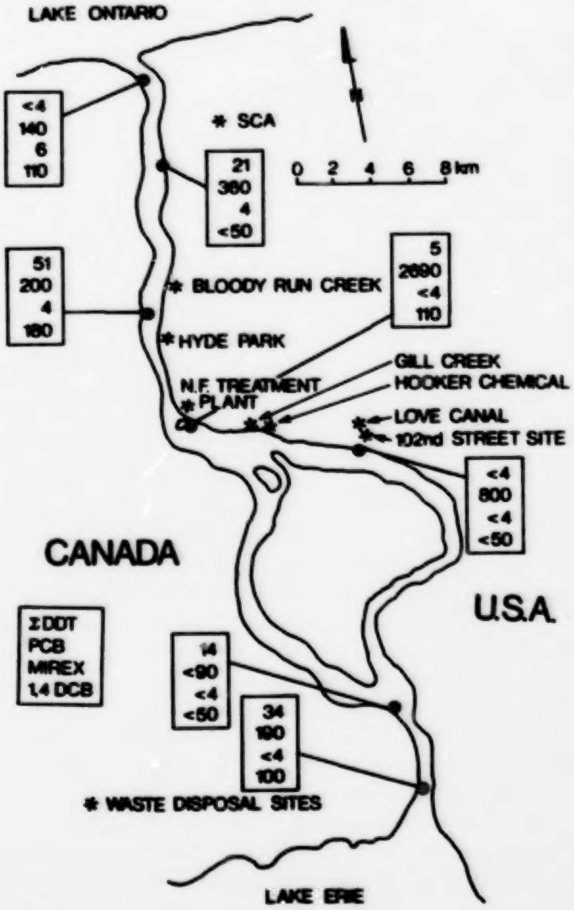
LAKE ONTARIO
<4
140
6
110
* SCA
21
380
4
<50
0 2 4 6 8 km
51
200
4
180
* BLOODY RUN CREEK
5
2690
<4
110
* HYDE PARK
N.F. TREATMENT
* PLANT
GILL CREEK
HOOKER CHEMICAL
LOVE CANAL
102nd STREET SITE
<4
800
<4
<50
CANADA
U.S.A.
ΣDDT
PCB
MIREX
1,4 DCB
14
<90
<4
<50
34
190
<4
100
* WASTE DISPOSAL SITES
LAKE ERIE

Figure 36. Organic contaminant concentrations in spottail shiners in the Niagara River (after Kuntz, 1984).

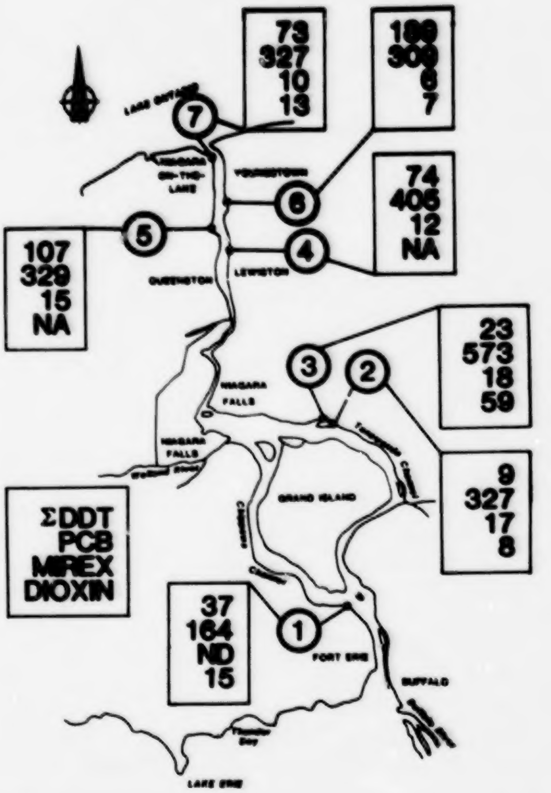
73
327
10
13
189
309
6
7
LAKE ONTARIO
7
NIAGARA-ON-THE-LAKE
YOUNGSTOWN
6
74
405
12
NA
5
107
329
15
NA
4
QUEENSTON
LEWISTON
3
2
23
573
18
59
NIAGARA FALLS
NIAGARA FALLS
GRAND ISLAND
9
327
17
8
ΣDDT
PCB
MIREX
DIOXIN
37
164
ND
15
1
FORT ERIE
BUFFALO
LAKE ERIE

Figure 37. Mean Σ DDT, PCB, mirex and dioxin (2,3,7,8-TCDD) residues in young-of-the-year spottail shiners in the Niagara River. The Σ DDT, PCB and mirex residues shown in nanograms per gram (1981) (after Suns *et al.*, 1983).

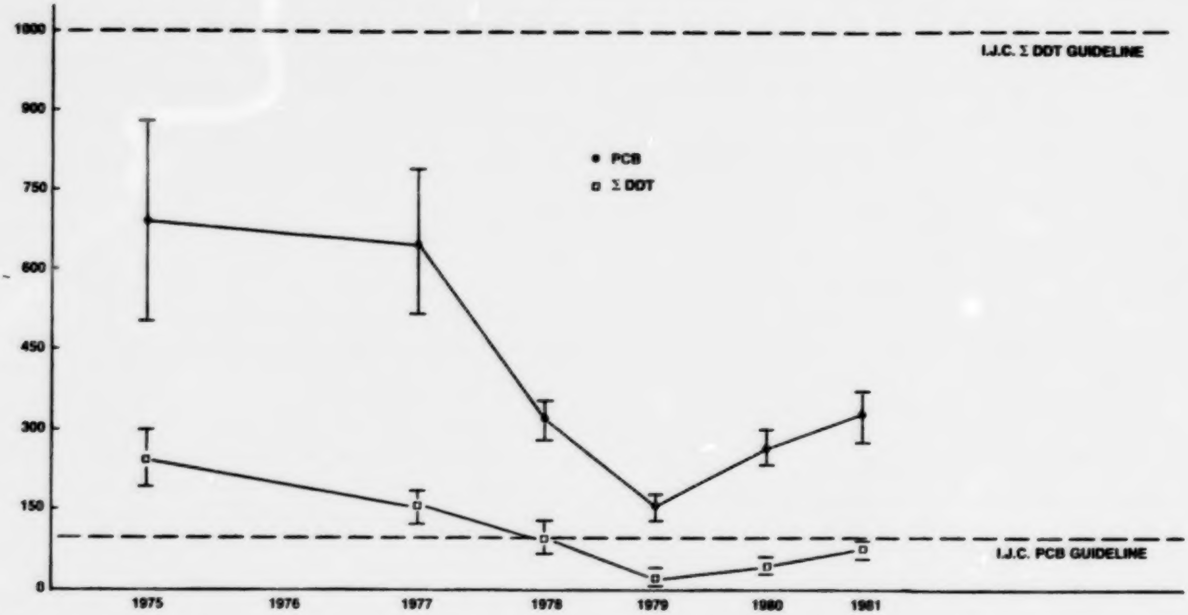

Figure 38. Mean PCB and **Σ** DDT residue trends in young-of-the-year spottail shiners (with 95% confidence limits) at Niagara-on-the-Lake (after Suns *et al.*, 1981).

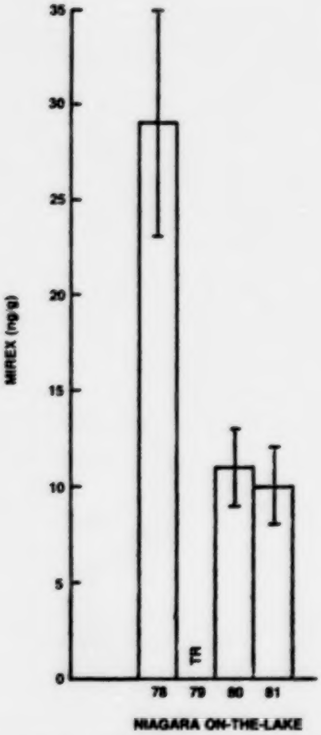

Figure 39. Mean mirex residues (with 95% confidence limits) in young-of-the-year spottail shiners from the Niagara River (after Suns *et al.*, 1981).

## BIOAVAILABILITY TO HERRING GULLS

In Lake Ontario, as in many aquatic ecosystems contaminated by organic chemicals, most chemical analyses were initially confined to bottom sediments and fish. Eventually, suspended sediments are collected and analyzed for monitoring and trend analyses. Because of problems with the hatching of herring gull eggs in the early seventies, a program began in the late seventies to analyze herring gull eggs to record contaminant trends. Herring gulls are fish-eating, and thus represented a higher "aquatic" trophic level than top predator fish. The results clearly demonstrate bio-accumulation to the top of the food web of several of the more hydrophobic and/or lipophilic organic chemicals with which various Lake Ontario pollution crises have been associated, namely DDT, then PCBs, mirex and now CBs and dioxins. Weseloh (1983) analyzed herring gull eggs from three colonies, above, on and below the Niagara River for three particulate-associated contaminants. For DDE and PCBs, concentrations were stable but for mirex, the most particulate-partitioned of the three, concentrations recently seem to be increasing (Table 12). The data do not suffice to draw definite conclusions on trends. What is shown is that for all three chemicals banned from use for several years, high concentrations are still found in the eggs of organisms at the top of food webs. Indirectly, this may again be evidence of the role of contaminated particulates in buffering improvements in pollution status by internal recycling processes. When external sources are severed, such

**Table 12. Mean Levels of Selected Contaminants in Herring Gull Eggs from the Niagara River and Nearby Monitor Colonies (ppm, wet weight)**

| Colony | Contaminants | 1979 | 1981 | 1982 |
|---|---|---|---|---|
| Lake Erie | DDE | 3.4 | 4.7 | 7.5 |
| | PCBs | 38 | 44 | 60 |
| | Mirex | 0.25 | 0.42 | 0.60 |
| Niagara River | DDE | 4.1 | 5.7 | 3.7 |
| | PCBs | 50 | 50 | 46 |
| | Mirex | 0.49 | 0.74 | 0.98 |
| Lake Ontario | DDE | 9.0 | 10 | 12 |
| | PCBs | 76 | 72 | 64 |
| | Mirex | 1.8 | 2.5 | 3.6 |

After Weseloh (1983).

long-term, slow improvements are not a problem with chemicals that are present almost exclusively in the aqueous phase, rapidly degraded in aquatic ecosystems or metabolized by higher organisms.

## BIOAVAILABILITY OF DIOXINS

In Lake Ontario, dioxins are the toxic chemicals of major concern in the early 1980s, as was mirex in the 1970s. In aquatic ecosystems, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) can be expected to follow the same basic environmental pathways as mirex. The $K_{OW}$ for TCDD, the most toxic of the many dioxin isomers, is around $1.4 \times 10^6$. A range from 1% to 100% organic content in sediments would result in partition coefficients of between $1.5 \times 10^4$ to $1.6 \times 10^6$. Suspended particulates in the Niagara River have a mean organic carbon content of around 10%. Given the suspended load of the Niagara, some 50% of TCDD should be present in particulate form. As explained in Part I, these can only be order of magnitude estimations because of the many assumptions and variations in limnological factors involved. For example, the organic content of suspended particulates, especially that related to summer primary productivity in a lake, has a major effect on the residence time of a chemical in the bioavailable pool.

Muir *et al.* (1983) compared the uptake of 1,3,6,8-TCDD by bottom sediment detrivores (*Chironomus* larvae and *Hexagenia* nymphs) and three sediment-burrowing species (Table 13). The sediments were spiked with 155 ng/g of 1,3,6,8-TCDD; flooded with water at a ratio of 7:1, and equilibrating for 48 h. The animals were either held in cups to obtain bioconcentration data from the water or were permitted to make contact with the spiked sediments. During the equilibrating period, the TCDD partitioned from the sediment to the water to nanograms per litre concentrations. All of the animals accumulated TCDD from both the water and sediment-water exposure routes. The chironomid larvae exposed to the sediment accumulated much higher body burdens of dioxins than the animals exposed only to water, presumably by desorption from ingested sediment. However, when the chironomid mouths were sealed, they still accumulated more dioxin, suggesting direct sorption through body walls from sediment pore waters. A sand sediment resulted in higher bioconcentration from the higher water concentrations that occurred when partitioning of dioxin into the sand was reduced. Silty sediments absorbed relatively more of the dioxin spike. Lower bioconcentration at higher water dioxin concentrations may have been caused by competition for the dioxin by colloidal material in suspension. Octachlorodioxin was bioaccumulated less than TCDD, perhaps owing to the higher molecule weight of the former or its higher suspended particulate (colloidal) partitioning.

In the Great Lakes, 2,3,7,8-TCDD has been detected in fish, bottom sediment and suspended sediment. Concentrations in all three can be as high as the low parts per trillion (5 to 20 ng/g) range and are considered high in terms of human consumption guidelines for fish. In most samples, 2,3,7,8-TCDD is beneath detection. It has been detected in whole water in the 10 ppq (pg/L) range, but this was most likely due to the presence of suspended or colloidal material. With a $K_{OW}$ around $10^6$ and a $K_{OC}$ for Niagara River

**Table 13. Accumulation of $^{14}$C-1,3,6,8-TCDD and $^{14}$C-OCDD by Several Aquatic Insects Following 96-H Exposure in Water and Sediment***

| Chemical | Animal | Water Conc. (ng/L) (ppt) | BCF† | | |
|---|---|---|---|---|---|
| | | | Water | Sediment (a) | Sediment (b) |
| TCDD | *Chironomus* | 44 | 1992 | 4682 | 1.3 |
| TCDD | *Hexagenia* | 29 | 2846 | 1879 | 0.4 |
| OCDD | *Chironomus* | 141 | 72 | 62 | 0.1 |

*Data for silty sediments only. Sandy sediments did not retain dioxin and resulted in very high water concentrations (hundreds of ppt).

†Water bioconcentration factor (BCF). Sediment (a) BCF for water and sediment exposed based on water concentration; BCF for sediment (b) was based on the sediment concentration rather than water concentration.

After Muir *et al.* (1983).

Table 14. Dibenzo-p-Dioxin Residues (pg/g) in Composite Samples from Lakes Michigan, Erie, Superior,* Ontario and Huron

| | Dibenzo-p-dioxin (pg/g) | | | | | Percent of 4-chlorines in total |
|---|---|---|---|---|---|---|
| Sample and site | 4† | 5 | 6 | 7 | 8 | |
| Lake trout | | | | | | |
| Saugatuck | | | | | | |
| (Lake Michigan) | 5 | ND | ND | ND | ND | 100 |
| Common carp | | | | | | |
| Saginaw Bay | 94 | 157 | 122 | 12 | ND | 24 |
| Bay Port | 27 | 21 | ND | 31 | 32 | 24 |
| Tittabawassee River | 81 | 31 | 44 | 53 | 14 | 36 |
| Herring gull | | | | | | |
| Saginaw Bay | | | | | | |
| Sample No. 1 | 160 | ND | 20 | ND | 19 | 80 |
| Sample No. 2 | 70 | ND | 88 | ND | 28 | 38 |
| (Lake Huron) | | | | | | |
| Common carp | | | | | | |
| Port Clinton | | | | | | |
| (Lake Erie) | ND | 9 | ND | 11 | 30 | 0 |
| Brown trout | | | | | | |
| Roosevelt Beach | | | | | | |
| (Lake Ontario) | 33 | ND | ND | ND | ND | 100 |

*No PCDDs were detected in Lake Superior samples.
†Number of chlorines.

ND – Not detected.

After Stalling *et al.* (1983).

suspended particulates of between $10^4$ to $10^6$, the predicted "aqueous" water concentration should be some 0.2 to 0.5 ppq (pg/L) which is still below detection limits, even in the largest water samples extracted to date. Dioxin concentrations in suspended biotic and abiotic particulates range over three orders of magnitude. In Saginaw Bay on Lake Huron, 2,3,7,8-TCDD has been measured in an outfall to the Tittabawassee River. The concentration in the river plume was 45 ppq, and fish caged in the river accumulated residues of up to 100 000 ppq 2,3,7,8-TCDD.

Fish are the biota most commonly analyzed for polychlorinated dioxins. There is extreme partitioning of dioxins onto particulates that are (1) sedimented but become food sources for benthic organisms which bioaccumulate the dioxins or (2) present in the water column as biotic particulates (bacteria, phytoplankton, zooplankton) and can be a direct food source to fish. Daphnids have bioconcentration factors for TCDDs of some $2.3 \times 10^4$ (Isensee and Jones, 1975). Benthic organisms and suspended biotic particulates can thus initiate passage of particulate-associated dioxins into aquatic food webs. Fillets of fish caught near the Canadian shores of the Laurentian Great Lakes and analyzed for 2,3,7,8-TCDD with a detection limit of 10 ppt produced positive results only in Lake Ontario, where values ranged from 11 to 26 ppt. The highest values were in lake trout. Stalling *et al.* (1983) analyzed fish from the Laurentian Great Lakes and related rivers for residues of PCDDs. A composite sample from the Tittabawassee River draining to Saginaw Bay contained 223 ppt of total PCDDs. The 2,3,7,8 isomers dominated (Table 14). They concluded that the lower concentrations of more highly chlorinated isomers were related to their lower water solubility and greater affinity for organic surfaces in aquatic systems and thus reduced bioavailability to higher organisms. A more complex answer could be that higher chlorinated toxic organic chemicals are

(a) Associated more with abiotic particulates and are more rapidly sedimented and buried

(b) Prevented from easy passage into biota by physical difficulties in penetrating cell membranes

(c) Excreted or metabolized to a greater degree by biota.

## CHAPTER 7

# Role of Particulates in Remedial Measures for Polluted Aquatic Ecosystems

Once an aquatic ecosystem has been polluted by toxic metals or persistent toxic organics, there are only limited options for remedial action, even if all remaining point source discharges or diffuse leachates can be eliminated. One reason for this is the continued recycling of sediment-associated contaminants. The bioavailability of the *in situ* pollutants becomes the critical parameter controlling the long-term recovery rate of the system. Part of the recovery can be natural and can be far more rapid than was predicted only a few years ago. Natural ways of recovery involve dilution, degradation of chemicals, volatilization, and other chemical breakdown processes which in some ecosystems can be enhanced by natural organics. However, the dominant particulate-associated recovery mechanism involves absorption or bio-uptake followed by settling and burial in bottom sediments in depositional basins of lakes or areas of fluvial sediment deposition. The efficiency of this process is recorded in sediment cores, and several examples of burial of toxic metals and organics are presented in Part I.

The system now most commonly used to decontaminate polluted systems is to dredge the polluted sediment and dispose of it elsewhere. The technique is drastic and usually very expensive. There are also problems with disposal of the spoil which, as mentioned earlier, has in fact been the impetus for research into toxic metal speciation in sediments and, more recently, bioassays for sediment-associated toxic organics. A less obvious amelioration technique is to accelerate the rate of burial by introducing more particulates into the system. This can be done *in situ* by

- (a) Deep dredging and redispersal of uncontaminated bottom sediments from beneath the contaminated surficial materials and
- (b) Introduction of uncontaminated particulates into the water column above the site of contamination.

When uncontaminated sediments are introduced into a water column, they will absorb contaminants according to the principles outlined earlier for toxic organics and in Part I for toxic metals. The result is that bioavailable contaminant fractions decline in the water column, although the total water column concentration may remain the same, or, with some metals, may even increase. Such a technique of sediment resuspension has been tested in enclosures by Rudd *et al*. (1984). They showed that additions of uncontaminated lake bottom sediments reduced bioaccumulation of mercury and selenium by zooplankton and crayfish (Fig. 40) and by fish. This technique has been proposed as a method of amelioration for the mercury-polluted Wabigoon River (Allan *et al*., 1984). When the resuspended particulates eventually settle out, surficial sediments will have lower toxic chemical concentrations and a lower bioavailable component in terms of exposure to benthic organisms.

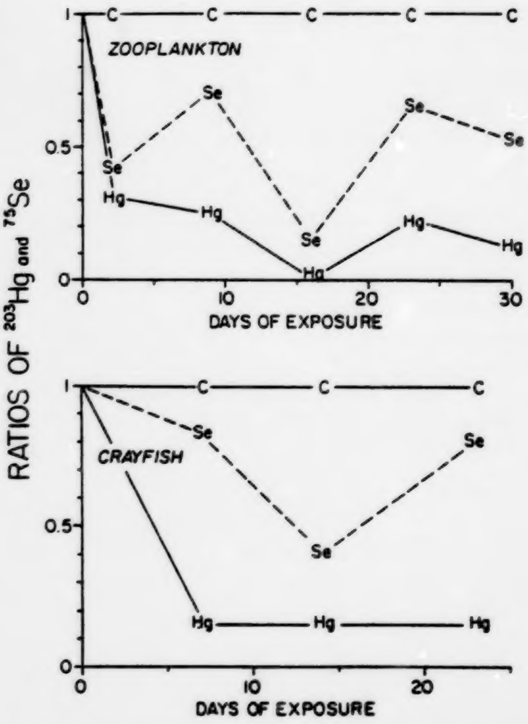

**Figure 40.** Inhibition of zooplankton (upper panel) and crayfish (lower panel), 203-mercury (Hg) and 75-selenium (Se) bioaccumulation by addition of inorganic-rich sediment to an enclosure. The data are expressed as ratios of $^{203}$Hg and $^{75}$Se activities in the suspended sediment enclosure divided by activities in the combined control enclosures (C) (after Rudd *et al*., 1984).

Another way by which particulate loads could be increased to accelerate settling and burial is by eutrophication or the addition of nutrients. Such increased productivity would reduce soluble concentrations of toxic chemicals. The biota produced, however, would be direct sources of food for higher organisms and the effect may be less than when abiotic particulates are resuspended. Alternatively, the same quantity of chemical would be diluted in the biotic material because of the higher productivity, and this could be reflected in lower bioaccumulation from food sources. Introducing competing ions is another method of reducing bioavailability. Rudd *et al*. (1984) demonstrated reduced mercury bio-uptake by adding selenium to limnocorrals in the Wabigoon River. Such interactions may involve colloidal species as discussed in Part I. There is also the possibility, as can be hypothesized from the data in tables presented here, of manipulating the food chain by causing species shifts or even by introducing new species to polluted aquatic ecosystems. Such techniques could interfere with bioaccumulation via the food web, even if the bottom sediment, particulate-associated, bioavailable contaminant fraction remained unaltered.

In summary, an assessment of the role of particulates in transport, burial, recycling, bioavailability and bioaccumulation is desirable at each polluted site prior to any attempt to ameliorate the pollution status of the system by any *in situ* technique.

# Conclusions

Several broad conclusions can be reached from the information presented here:

1. Species changes of metals to more toxic organometallic forms result in recycling into the water column from bottom sediments and an increase in relative bioavailability and bioaccumulation.

2. Steady state levels of contaminants in polluted river waters indicate re-establishment of equilibria between bottom sediments and water, with possible volatilization of compounds at the water/air interface.

3. Chemical release of toxic organic contaminants from bottom sediments is suspected but has not yet been investigated by sequential extraction techniques. Apparently, all hydrophobic compounds can be completely extracted from the sediment fraction by water alone, if sufficient time is available.

4. Biological laboratory techniques for assessing sediment toxic organic chemical content are widely employed and show that a variety of benthic organisms and near-bottom filter-feeding organisms bioaccumulate toxic organic chemicals from sediments. The chemicals are bioavailable to varying degrees to different organisms. It is not clear how much of this is due to bottom sediment-pore water equilibria; pore water-overlying water equilibria; or direct stripping of chemicals from particulates by biota.

5. Biological processes of bottom sediment-mixing (bioturbation) recycle toxic organic chemicals through direct uptake by benthic biota and through physical disturbance or feces deposition. The depth and degree of mixing by various organisms are seldom quantified but are important parameters requiring quantification in real polluted aquatic ecosystems, if the rate of recovery is to be modelled and predicted.

6. Physical resuspension, usually event-related, of bottom sediments in rivers and in lakes is a demonstrated recycling pathway for particulate or pore water-associated toxic compounds. Resuspension occurs even in very large lakes.

7. The introduction of uncontaminated particulates nearly always increases the amount of a toxic chemical that can be present in the water without being toxic to some aquatic biota, although this may not be true for filter feeders and bottom-dwelling benthic organisms.

8. Soluble toxic organic chemicals are rapidly flushed from aquatic ecosystems when all sources are controlled. Alternatively, more hydrophobic, more particulate-associated toxic organic compounds, those often sedimented near sources or in downstream lakes and improvements, remain in aquatic systems after external sources are removed. In the short term (decades), these chemicals are subject to chemical, physical and biological internal recycling and bioaccumulation into food webs.

## CHAPTER 9

# Research Needs

Research to resolve the transport, burial, recycling, bioavailability and bioaccumulation of contaminants is needed to understand how toxic metals and organics are cleansed naturally from aquatic ecosystems or become concentrated in media and result in exposure to and hence risk to aquatic biota and humans. Extensive resources and integrated research activities are needed. Research activities should not be limited to convenient areas of expertise or disciplines. The areas that most need to be researched are the interfaces between the broad limnological, chemical, physical and biological sciences. We cannot measure all chemicals in all media at all sites. Models for predicting the environmental fate of toxic metals and organic chemicals are often based on laboratory research which provides information on rates of reactions. Although these models can predict compartmentalization on a gross scale, they often fall afoul of the complexities of natural ecosystems. They usually cannot predict concentrations in specific media, and concentrations are required for estimation of real risk.

Data bases need to be extended to include many intermediate food web biota. More sites will need to be studied and sampling frequencies will have to increase. A more flexible, contaminant-oriented sampling of aquatic media should aim at providing not only a monitor of conditions but a more readily interpretable data base for bioavailability and bioaccumulation processes. In summary, there is a need for

1. More data at specific polluted field sites if we are to understand pathways and produce realistic predictive models of contaminant fate
2. More concentration data on lower trophic level biota, different types of benthic organisms and phyto- and zooplankton species
3. More information on food webs to ensure enough concentration data for all media and biota relevant to exposure to higher organisms and humans
4. More information on the nature of the suspended load, with biotic and abiotic component separation and analyses
5. Better detection limits in water for some of the more serious chemical isomers, e.g., the dioxins.

Lee *et al*. (1982) reviewed the significance of pesticide residues associated with aquatic sediments from the viewpoint of acute toxicity of dredge spoils released to the water column and made three points applicable here:

(a) There is no relationship between the total concentration of a pesticide in a sediment and the tendency for the sediment to release pesticides upon resuspension.

(b) The introduction of sediment nearly always increases the amount of pesticide that can be present without being toxic to aquatic life, although this may not be true for filter feeders.

(c) The impact of sediment-associated contaminants and their bioaccumulation by benthic and epibenthic organisms must be further researched.

Research must focus on processes. Laboratory studies have already provided valuable clues to how real systems may operate. Laboratory studies of bioavailability will need to go beyond the approach of simply measuring bio-uptake to explaining processes of uptake. More complex real environmental factors, such as biota excretion rates or the influence of periphyton on rates of degradation, will have to be quantified. Research at polluted sites requires input, not only from chemists, geochemists and biologists but, for a complete understanding of fate, also from biochemists and physicists, hydraulic engineers, hydrogeologists and hydrogeochemists. Atmospheric scientists need to become involved because of the role of gaseous, wet and dry precipitation and volatilization on the ultimate fate of many organometals and persistent organic chemicals. Limnologists or those with training in lake, river and impoundment processes must also apply their expertise. In fact, nearly all those specializing in the disciplines above need to develop adjunct expertise as limnologists, if they expect to begin to resolve true environmental pathways and fate of contaminants.

The questions central to the toxic chemicals issue are broad: Can I safely drink the water? Can I eat the fish or other aquatic biota? Can I swim in the water? Why is the river/lake system polluted? Why is this ecosystem's health degraded? What is a stressed ecosystem? Can I dredge sediment from this aquatic ecosystem and where can I put the dredged material? Research needed to begin to make intelligent responses to such questions includes:

(a) new approaches to setting aquatic ecosystem objectives in which aquatic toxicity testing takes the influences of the organisms themselves into account

(b) laboratory testing of chemical properties and toxicity testing of mixtures of toxic metals, organics and combinations thereof

(c) a complete understanding of the pathways, fate and effects of pollutants in real aquatic ecosystems, including the critically important role of particulates in transport, burial, recycling, bioavailability and bioaccumulation of toxic contaminants.

The research encompassed in studying the transport, burial, bioavailability (recycling and bioaccumulation) of contaminants has one overall purpose. The purpose is to understand how toxic metals and organics are removed from aquatic ecosystems or how they become concentrated in media and result in environmental or human exposure (total ecosystem exposure) and hence risk. Obtaining the basic data to calibrate models is expensive and time consuming. Analyses of a few bottom sediments, sediment cores, or fish samples only shows that a contaminant problem exists, not necessarily what it means (risk) or what to do about it (control, amelioration). To make the connection between transport and burial phases, recycling and bioavailability processes, and bioaccumulation mechanisms requires a large data base. Such data bases have not yet been satisfactorily acquired. For the myriad organic chemicals, the minimum requirement is to resolve the aquatic fate of selected groupings of chemicals with a range of physico-chemical properties in a range of polluted ecosystem types: low/high suspended particulate load rivers; low/high suspended particulate load lakes; oligotrophic/eutrophic lakes; deep/shallow lakes; low/high pH rivers and lakes. Even in Lake Ontario, a site studied in some detail over a five-year period, we are still far from modelling the fate of more than a few chemicals in a very rudimentary way. A major deficit is extensive information on the biological distribution of contaminants. This deficit is partly due to difficulty in collecting enough of the lower trophic level biota for analyses or the tediousness of obtaining meaningful information on such things as fish stomach contents. There are gaps of knowledge on chemical levels and transfers between critical compartments that may play central roles in contaminant-particulate interactions. Models for contaminant fate prediction must be sophisticated. Predicting the fate of a contaminant in a specific aquatic ecosystem requires knowledge of: all inputs (loadings from tributaries, the atmosphere, bottom sediments, point and non-point sources); initial conditions (concentrations of all relevant media at specific times); process pathways and rates (of transport, volatilization, photolysis, hydrolysis, degradation, sedimentation, burial, resuspension and bioaccumulation).

Contaminant concentrations in surficial sediments often include the benthic component. In suspended particulates the plankton is usually included because of operational necessity. Colloidal particulates are ignored or become part of the operationally defined aqueous phase. We need to refine our ability to separate and investigate these components of whole water. We may have far more surficial bottom sediment-contaminant concentration data than we need, yet there are few core analyses with subdivisions fine enough for resolution of changes in contaminant loads over short time periods. Of course, most contaminant data were not collected as input to complex predictive models, but as a means of detecting sources and measuring the degree and spatial distribution of contamination. Standard chemical parameters and properties ($K_{OC}$, $K_{OW}$, solubility) provide insight into the fate of chemicals of major compartments. However, non-equilibrium reactions such as food-chain transfers dominate in real aquatic systems. Critically important, extensive experiments of the type conducted in limnocorrals to resolve Hg bioaccumulation in the Wabigoon River may be needed to quantify food-chain transfers and related rates of bioaccumulation and depuration.

Although toxic metal research was well established by the late seventies, only in the early eighties have we seen organizations apply to toxic organics the many laboratory and field research techniques formerly used to investigate toxic metal problems in aquatic ecosystems. In fact, we have only now begun to comprehend the real complexity of contaminant fate in aquatic ecosystems. As in any field of research, there have, of course, been lone individuals ahead of their time. We do have considerable information on concentrations in various aquatic media and on distributions and transport phases in isolated systems. However, perhaps because of the capital costs involved or the complexity of the research, much of the information is disjointed. There has been a tremendous increase in collective knowledge of the chemical pollution status of aquatic ecosystems over the past ten years for toxic metals and the past five years for toxic organics. It is now important to extend to new levels of understanding the factors and processes controlling the fate of persistent toxic organic chemicals in aquatic ecosystems because, even with the environmental pollution controls now in place in developed nations, pollution remains a problem. There are still many point sources of continued effluent input to aquatic ecosystems and there is a continued pressing need to dispose of toxic chemical wastes. More extensive use of toxic chemicals (biocides) in agriculture and forestry, industrial and urban development, and extension of these pollutant problems to the third world by foreign trade could result in a global problem, for which the ability to predict the aquatic fate and effects of toxic contaminants becomes a critical requirement.

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